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Deleterious Properties of Chert

INTERIM REPORT

PHYSICAL RESEARCH PROJECT NO. 12

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DECEMBER, 1962

ERRATA

Page 11, add Fig. 7 above page number.

Page 71, 4th paragraph, last sentence, last word. Change APPENDIX B to APPENDIX A.

Page C-2, 2nd paragraph, last sentence. The words in parentheses should read (Table 6, and Figure 15).

Page E-1, between 1st and 2nd paragraphs. Add arrows so that equations read:

$$MgCO_3 + 2NaOH \longrightarrow Mg(OH)_2 + Na_2CO_3$$

$$CaMg(CO_3)_2 + 2NaOH \longrightarrow Na_2CO_3 + Mg(OH)_2 + CaCO_3$$

DELETERIOUS PROPERTIES OF CHERT

Physical Research Project No. 12

Conducted by

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for

Rensselaer Polytechnic Institute
Troy, New York

Under Research Contract No. HC-5360
With the

New York State Department of Public Works
In Cooperation With
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Bureau of Public Road

Bureau of Physical Research

December, 1962

ABSTRACT

Deterioration of portland cement concrete pavements and structures made with aggregates containing chert has been extensively reported. The cause of the distress is generally attributed either to a chemical reaction between the chert and alkaline solutions formed during the hydration of the portland cement or to rupture caused by freezing and thawing of water in the voids of certain types of porous cherts.

Evidence of abnormal expansion in the form of "pop-outs" and map cracking has been noted in central and western New York. The use of chert-rich Onondaga limestone in much of the distressed concrete suggested that the chert may be linked to the cause of the distress. The present study is an investigation of the cherts in the Onondaga limestone formation of central and western New York to determine the likelihood of deleterious effects in portland cement concrete.

The cherts occurring in the Onondaga formation between Jamesville, and Buffalo, New York, were studied both in the field and in the laboratory. Fresh bulk samples and rock cores were obtained from selected stratigraphic intervals at several locations, most of which were active quarries.

The cherts were classified into nine working groups based on field occurrence, appearance, and megascopic properties. The areal and stratigraphic location of these chert types within the formation were mapped, and their mode of occurrence and relationship to the limestone illustrated and summarized.

Chemical, x-ray, and petrographic analyses indicate that all the cherts consist chiefly of silica in the form of microcrystalline quartz with small amounts of calcite and dolomite. The percent of lime in the cherts was found to be inversely proportional to the percent of silica.

Although consisting essentially of quartz, the specific gravities of the cherts, as determined by several methods, were found to be appreciably less than that of quartz. With only one exception, the water absorptions of fourteen cherts tested were zero or very low. The relation between the mineralogy of the chert and properties causing depressed specific gravity is discussed.

The potential alkali-reactivity of selected cherts was investigated by the quick-chemical and mortar-bar expansion tests. The results of the quick-chemical tests are discussed with respect to reproducibility, pessimum proportion, and the "carbonate effect." Mortar-bars containing varying percentages of chert were examined megascopically and microscopically, and the results of the tests compared with quick chemical, and other determinative and descriptive test results. The relation between the microscopic texture of the cherts and their quick-chemical and mortar-bar behavior is discussed, and a hypothesis presented to account for the unexpected reactivity of cherts composed essentially of quartz.

The results of the investigations completed to date permit the following major conclusions:

(1) All cherts are potentially reactive according to the standard interpretation of the ASTM "quick-chemical" test.

(2) Five of the six cherts tested are deleteriously expansive when combined with high-alkali cement according to the standard interpretation of the ASTM mortar-bar test. However, it should be noted that until similar tests are conducted on concrete made with the chert and the natural limestone in which the chert occurs[1], the concrete distress in the central and western part of the state cannot definitely be ascribed to alkali-aggregate reactivity.

(3) The smaller expansion of the sixth chert (which did not exceed the allowable 0.1% expansion) is attributed to porosity, as evidenced by relatively high water absorption, which may "relieve" expansion by absorption of gels which result from alkali-reactivity. However, porous cherts with dull luster, such as these, may be more susceptible to freeze-thaw deterioration.

(4) Cherts composed essentially of microcrystalline quartz are capable of a deleterious degree of reactivity.

(5) The most potentially deleterious cherts studied in this investigation are characterized by high silica contents, low carbonate contents, and variable texture and grain size. These characteristics contrast with those of the least potentially deleterious cherts.

(6) The concentrations of chert which had maximum expansion in the mortar-bar test on six cherts were: four at 50% chert, one at 10% chert, and one at 20% chert. However, the most expansive cherts had excessive expansions (greater than 0.1%) over a range of concentrations from 10% to 70% chert.

(7) Sands and gravels which are derived from weathered Onondaga cherts should be considered alkali-reactive.

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[1] Mortar-bar expansion tests in this research were conducted using the standard procedure of diluting the investigated aggregate with quartz. This procedure is an expedient which eliminates certain variables and allows results to be compared, but it does not reasonably reproduce the natural environment of concrete fabricated from this chert-bearing limestone.

ACKNOWLEDGEMENTS

This research was conducted by the Geology Department of Rensselaer Polytechnic Institute, Troy, New York, under contract with the New York State Department of Public Works, in cooperation with the U. S. Department of Commerce, Bureau of Public Roads, under the State-Federal Physical Research Program.

The investigation was suggested by Mr. Paul Bird, Senior Engineering Geologist of the Bureau of Soil Mechanics, who was also consulted for technical assistance and counsel in various phases of the investigation.

Participating personnel at R. P. I. were Prof. James R. Dunn (Senior Investigator), and Michael A. Ozol (Research Assistant).

The X-ray diffractometer was operated by Ronald G. Senechal, and his assistance is gratefully acknowledged. Dr. Donald S. Miller provided valuable advice on some laboratory procedures.

Personnel of the New York State Bureau of Physical Research coordinated the work, assisted in the preparation of samples for testing, conducted the mortar-bar tests, assisted in laboratory work at R. P. I. and assisted in editing the report. The New York State Bureau of Materials provided laboratory facilities and conducted chemical analyses, and quick-chemical tests.

All quarry operators cooperated fully in permitting observation and collecting of samples in their quarries. Their assistance is gratefully acknowledged.

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INTRODUCTION

Chert is commonly composed of various fine-grained silica minerals occurring as opal, chalcedony, quartz, or other forms of silica. According to Sweet (26)*, cherts have been found in rock formations of almost every geologic age and are most frequently associated with limestones, dolomites and chalk. They occur as distinct layers or as isolated nodules within the parent limestones. Chert has been found in many parts of the United States, but it is particularly plentiful in the west and mid-west.

In New York, the Onondaga formation (Devonian) is the only aggregate-producing formation which contains large amounts of chert. In addition, it is the most productive limestone formation in the state, as evidenced by the fact that it is being worked in at least seventeen quarries. The chert content of the Onondaga formation increases from east to west; fifty percent or more being common in some stratigraphic intervals in the extreme western portion of the state while much lesser amounts occur east of Jamesville.

Before 1940 the belief that chert was a chemically and physically inactive rock was shared by many engineers. Experience has shown, however, that certain types of chert have a deleterious effect in portland cement concrete. Numerous studies have defined two general modes of deterioration of portland cement concrete containing chert in the aggregate. Particularly common in concretes containing weathered cherts are failures caused by the alternate freezing and thawing of water in the voids of the chert. Damage results from the dilation of the cement paste or dilation and breakage of aggregate particles, or from both. Often, the first signs of deterioration are in the form of pop-outs and D-cracking. Typical of the work done on this subject is the investigation by Sweet and Woods (27). Another mode of distress has been traced to a reaction between certain cherts and the strongly alkaline solutions which are formed during the hydration of portland cement. This reaction produces an alkali-silicate gel-like substance which expands on contact with water. The result is excessive expansion of the concrete accompanied by map cracking. These cracks allow water to permeate the affected concrete and thus make it susceptible to further damage by freezing and thawing. One of the earliest investigators of this problem was Stanton (24), (25) whose studies of concrete deterioration in California have become classical references.

*Numbers in parenthesis refer to items listed in the Bibliography.

Background

Considering the widespread geographic occurrence of chert, it is not surprising that concrete disintegration from these causes has been discovered over a large portion of the country. All cherts, however, are not deleterious. While many cherts have been derived from the same geologic system, their physical and chemical properties may vary widely. Aware of this, many highway departments have conducted comprehensive studies of the cherts occurring in their respective states. Many states have resolved the freezing and thawing problem by limiting the amount of chert allowed in the aggregate. Those affected by the alkali-aggregate reaction have adopted specifications which limit the amount of chert or the maximum alkali content of cement, or require the use of an additive to "neutralize" the reaction. In contrast, no special requirements have ever been incorporated in the New York State Department of Public Works Specifications because, although the occurrence of chert in quantity has been known for many years, failures in the state due to the presence of chert have never been documented.

Recently, unusual forms of deterioration have been noted in concrete pavements in the central and western parts of New York. While the major cause of distress appears to be physical in nature, as evidenced by "pop-outs," the appearance of map cracking suggests that a cement-aggregate chemical reaction also has occurred. Since these observations have been made in a section of the state where chert is found in quarried aggregates, it is logical to suspect that some varieties of chert may be the cause of the deterioration.

Purpose

The objective of this program has been to investigate the various types of chert appearing in the Onondaga limestone formation within the general area between Jamesville and Buffalo to determine whether any deleterious properties are inherent in the cherts encountered.

Scope

This study is based on an examination of bulk samples of chert-bearing limestone obtained from the operating faces of quarries and, where possible, supplemented by rock cores. The field work involved sampling, establishing the areal and stratigraphic distribution of the cherts, and describing the mode of occurrence and relationship of the cherts to the parent rock. Laboratory studies involved petrographic and binocular examinations, x-ray diffraction analyses, electron microscopy of surface textures, specific gravity and absorption tests, chemical analyses, and ASTM quick-chemical and mortar-bar tests. Also in progress, but not included in this interim report, are permeability, freeze-thaw durability, sulfate soundness, thermal expansion and additional mortar bar tests. A final report summarizing all of this work, including other special studies being conducted by the Bureau of Physical Research, will be prepared at a future date.

Field Studies

Logging and Recording of Stratigraphy

Thirteen quarries in the Onondaga formation were investigated and lithologic logs plotted for them on a scale of 1" equals 1'. These logs served as a basis for preparing the reduced logs which appear in the correlation chart (Figure 9). ("Stratigraphic Correlation and Sample Intervals"). Field work was largely confined to exposures in quarries, but road cuts and stream outcrops were used when available and as required to supplement information obtained in quarries.

Stratigraphic sections were recorded on a bed by bed basis. Every chert bed or zone of nodules encountered was measured and described. Particular attention was given to shape, dimensions, distribution, and quantity of types of chert. The percentage of chert occurring in a stratigraphic interval was estimated by two methods:

(1) Where cherts occur in a layered or bedded fashion (Figure 4) or in an anastomosing network, (Figure 2) a steel tape or ruler is placed against the rock face perpendicular to the bedding and the ratio of inches of chert vs. inches of limestone noted. The average of several determinations whose positions are random is used to indicate the percentage of chert within the interval.

(2) Where chert is more sparsely distributed and occurs as nodules outcropping along a horizon (Figure 1), the percentage of chert is estimated by inspection in the manner of the petrologist noting the percentages of mineral components in a hand specimen. However, the method described in (1) above is used as a check.

Sampling

Three types of samples were utilized in the course of the investigation:

(1) Hand specimens oriented with respect to top and bottom were collected from and keyed to specific beds. These supplied material for thin-sections and megascopic study slabs.

(2) Diamond drill cores (NX, 2-1/8" diam.) taken specifically for this project provided supplementary data on thicknesses of units and stratigraphy. Megascopic study slabs and thin-sections were also made from selected intervals of the core.

(3) Bulk material blasted in the course of the normal quarrying operation was used wherever large quantities of sample needed to be concentrated for a particular test, e.g. the mortar-bar expansion test. Material from these samples was also used for tests requiring smaller amounts of material. (See: Preparation of Samples for Testing).

a. Two horizons of large simple nodules in massive limestone at location #55, just above Tioga bentonite (shaly zone just above lower edge of photograph). Not sample #55.

b. Compound "white" chert nodules in massive limestone at location #55. Chert shown is sample 555.

Fig. 1. SIMPLE AND COMPOUND CHERT NODULES IN MASSIVE LIMESTONE

a. Ragged anastomosing chert (light colored) in massive, medium to coarse grained, limestone at location 43. Not sample 43-B.

Scale: Shown by steel tape.

b. Ragged anastomosing chert (dark colored) in massive, medium to coarse grained, limestone at location 43. Not sample 43-B.

Scale: Shown by ruler.

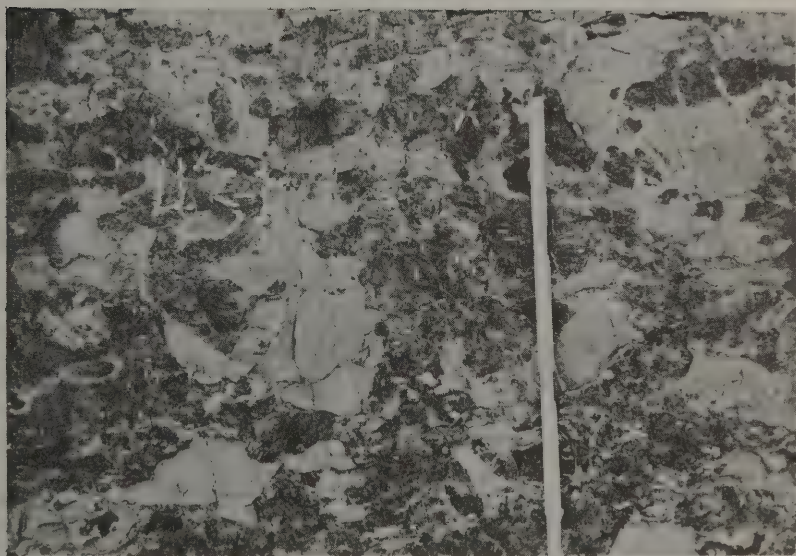
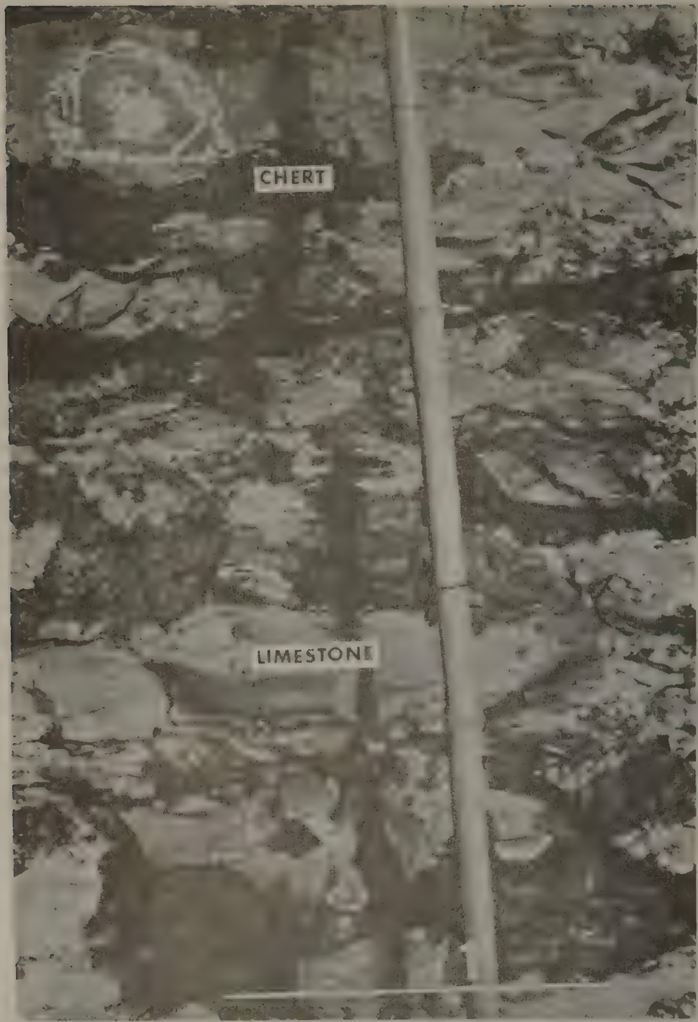
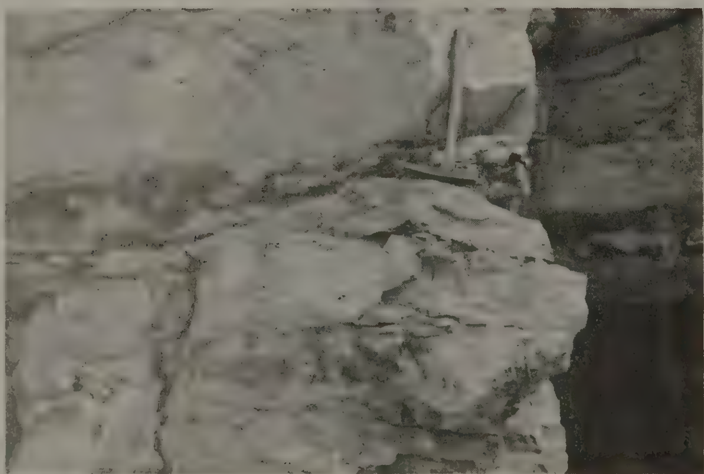


Fig. 2. RAGGED ANASTOMOSING CHERT IN MASSIVE LIMESTONE



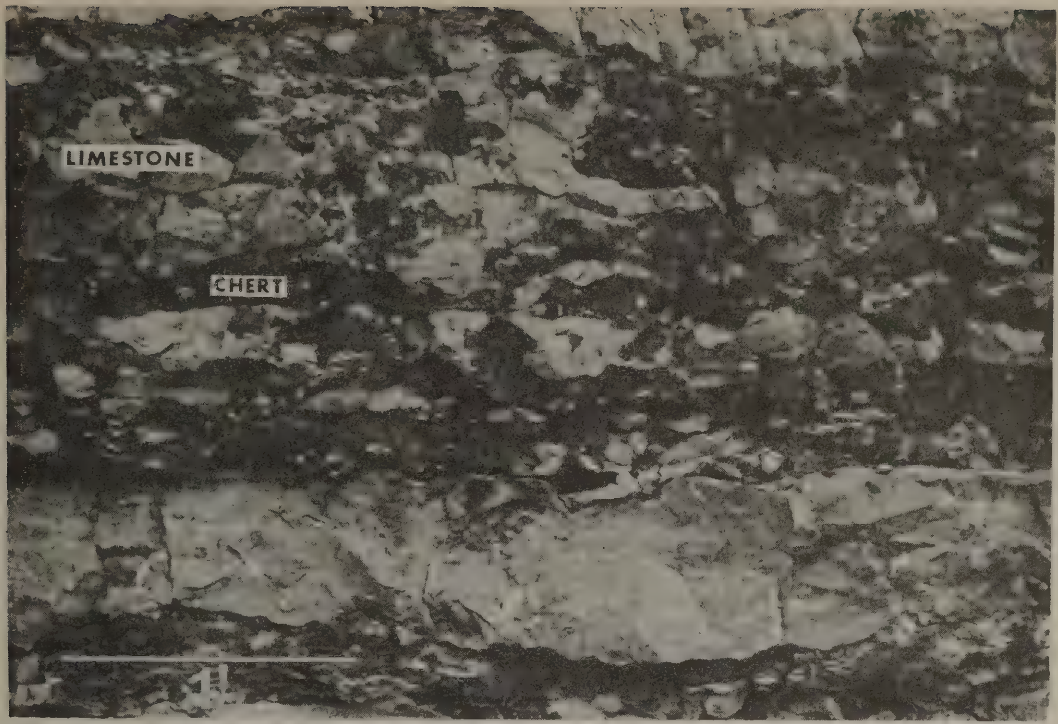
a. Irregular chert nodules slightly anastomosing between "beds." Abandoned quarry, Akron, New York.



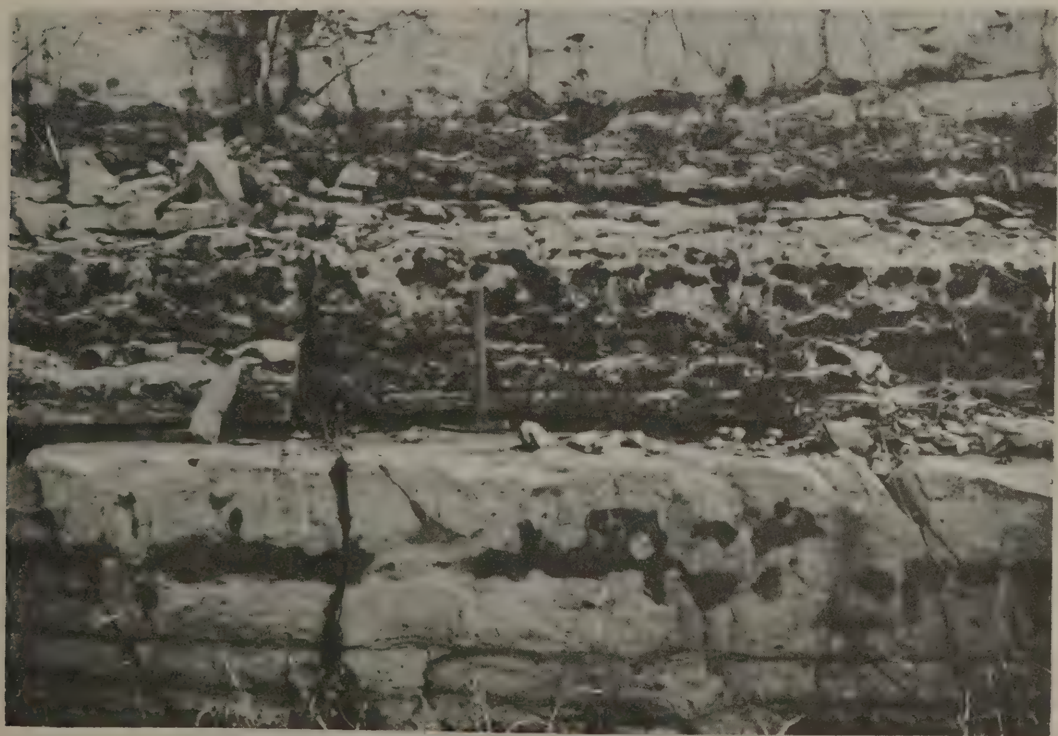
b. Irregular chert nodules (dark) maintaining fairly evenly bedded relationship at location 44.

Scale: Shown by hammer.

Fig. 3. IRREGULAR CHERT NODULES



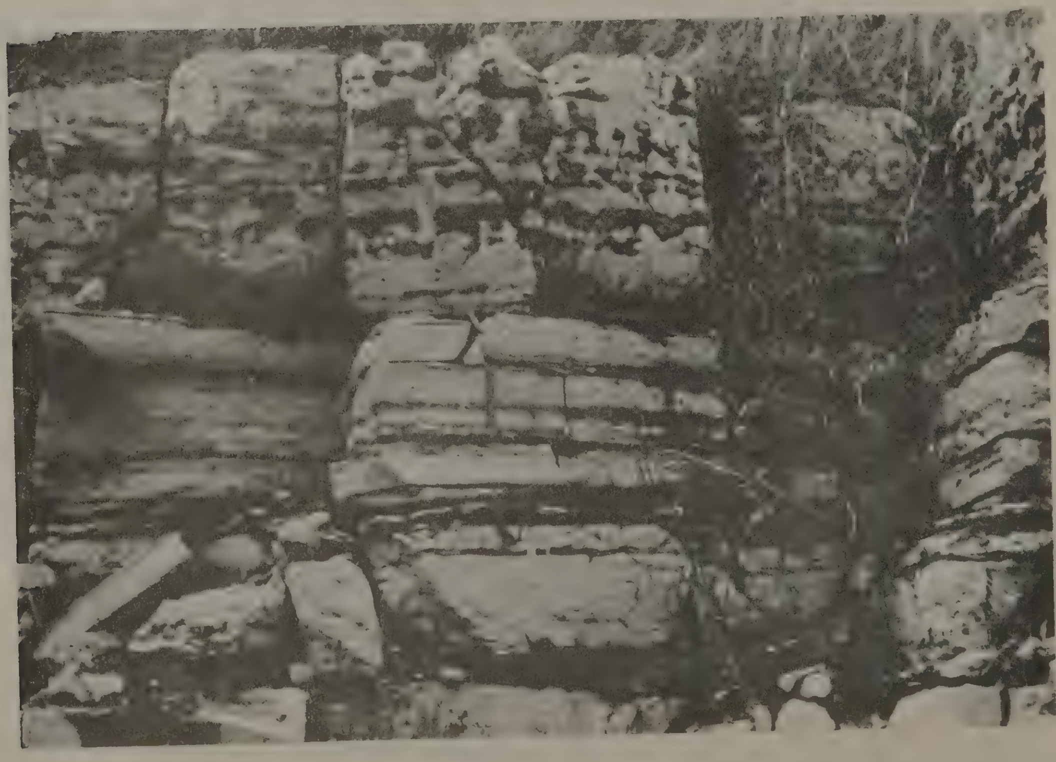
a. Chert interbedded with fine-grained limestone (broad band across upper 2/3 of photograph). Location 43.



Interbedded chert and limestone (broad band across center of photograph), in which the limestone is subordinate. Note horizon of compound nodules just below "11" in photograph. Scale: Indicated by hammer. Location: Vicinity #42.

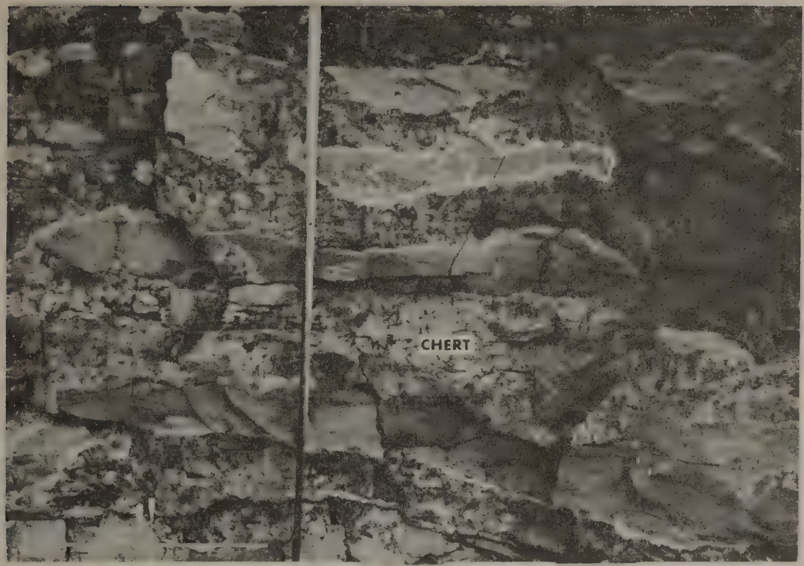
Fig. 4. INTERBEDDED CHERT AND LIMESTONE

a. Persistent bed or seam of chert (arrow). Location 45

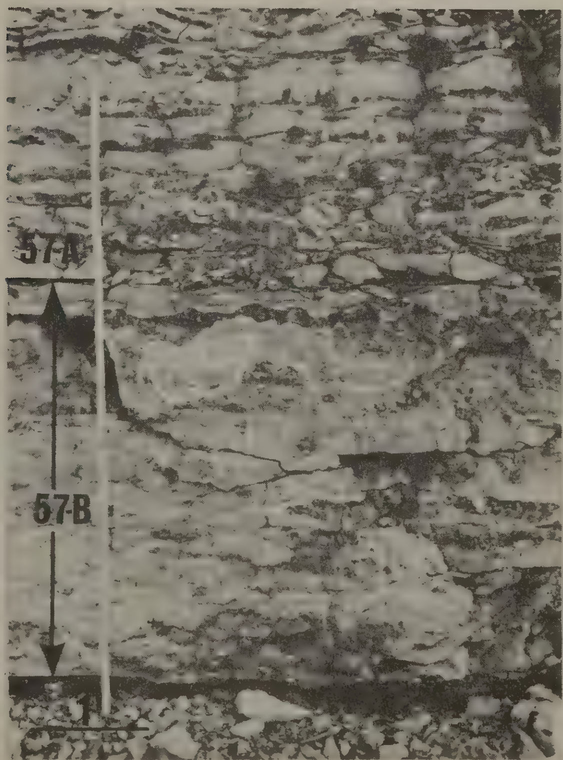


b. Horizons or "beds" of compound nodular cherts in massive limestone at location 37. Note the slight migration of nodules between planes.

Fig. 5. SEAM AND BEDS OF CHERT



a. Detail of sample zone 57-B showing intermixed chert and limestone in which the limestone may occur as islands within the chert. An island of limestone is outlined (Ls. 57).



b. Sample zone 57-A: Thin lenses or stringers of dark chert in fine grained bedded, limestone. The top of sample zone 57-A is not shown.

Sample zone 57-B: Intermixed chert and limestone; irregularly bedded anastomosing chert in massive, medium to coarse grained limestone.

Fig. 6. INTERMIXED CHERT AND LIMESTONE

Selection of Samples for Testing

The selection of particular cherts for testing by the quick-chemical and mortar-bar methods was based on compromises between the following considerations:

(1) A range of chert types of contrasting megascopic properties (color, luster, fracture, etc.) should be represented.

(2) A range of chert types with contrasting modes of occurrence (bedded, nodular, anastomosing, etc.) should be represented.

(3) The selection should include a range of chert types which is geographically and stratigraphically representative.

(4) A range of cherts of contrasting chemical and mineralogic properties should be represented. Note: Complete, detailed information on chemical and mineralogic constitution was not available at the time the selection was made. The properties referred to are those which could be deduced by various simple tests.

(5) Relatively more abundant chert types should be given preference.

(6) The chert samples selected should be in stratigraphic intervals which are accessible for the collection of large quantities of material.

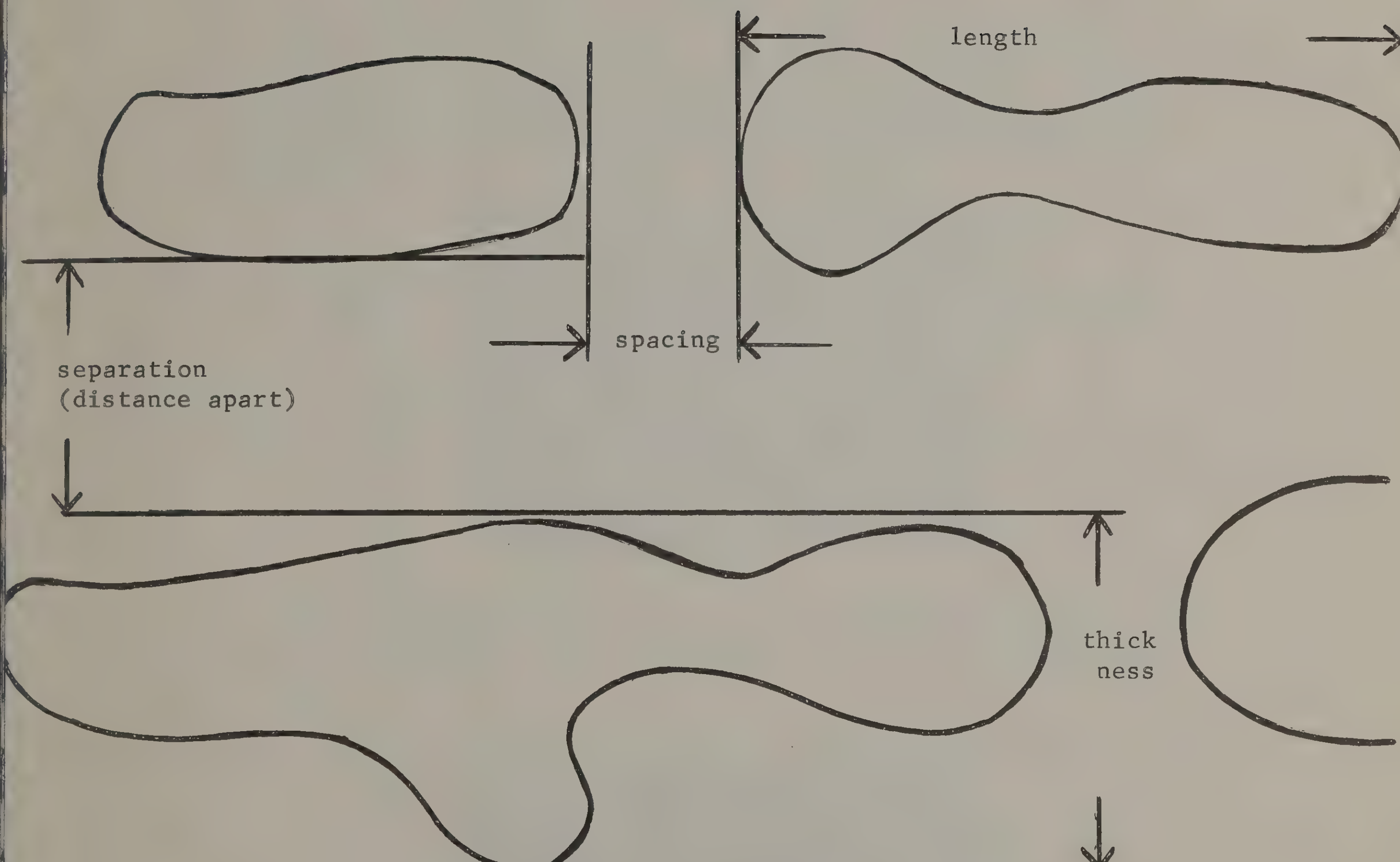
Description and Tabulation of Chert Samples

The megascopic descriptions of the cherts which appear in the following tabulation were prepared by use of the hand lens and binocular microscope. Study slabs of chert in limestone matrix were stained and etched to emphasize textures and the distribution of components.

The colors used in the descriptions are defined by the Rock Color Chart (7). The terminology used in describing the dimensions of chert nodules is presented in Figure 7. Figures 1 through 6 illustrate various modes of occurrence of the chert in the limestone matrix.

The megascopic descriptions include the presence of "rim" or peripheral zones around some cherts. The detailed petrology of these zones will not be discussed, but they may be briefly described as follows:

TERMINOLOGY USED IN DESCRIBING SIMPLE AND COMPOUND NODULAR CHERTS

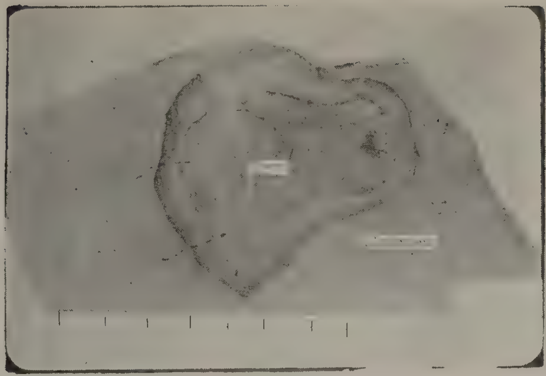


Between the interior of the chert nodule and the enclosing limestone (see Figure 8), certain cherts exhibit a rim zone surrounding the nodule which may be distinguished by its lighter color and duller luster (etching and staining will make the zone very pronounced). The zones are usually thin (1/4" to 1/2") in comparison with the diameter of the nodule, but thicker cherts commonly have thicker peripheral zones. Staining tests and petrographic examination shows that the chief mineralogic difference between the rim zone and the chert is the higher percentage of dolomite in the zone. Chemical analyses of a chert and its zone (Table 3, columns 45C and 45R) indicate that the zone (45R) is lower in silica, but richer in lime, magnesia, and CO_2 than the chert (45C).

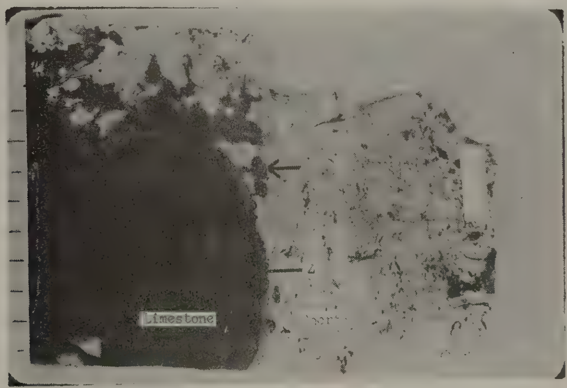
Occasionally, "zone-type" material of similar petrographic and chemical properties may also occur in irregular patches within the chert nodule (or bed, or stringer, etc.) and also within the adjacent limestone.

In the following tabulation (Table 1), the chert sample number is keyed to the correlation chart (Figure 9) and the map showing sample locations (Figure 10). The stratigraphic position and continuity of each chert sample zone may be found by reference to the sections on the Correlation Chart.

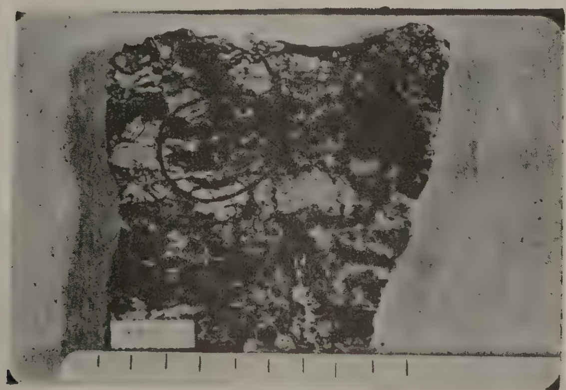
Six cherts were selected for fabrication into mortar-bars and these will be referred to as the primary test group. They are indicated by an asterisk on the tabulation chart. Three more cherts were fabricated into mortar-bars at a later date, but complete discussion of the mortar-bar performance of these must be deferred. These latter three were, however, included in all the associated tests such as X-ray, chemical analysis, specific gravity, and others, and certain conclusions on the basis of that information may be drawn relative to them.



a. Simple nodular chert with peripheral zone, or rim, between interior of chert nodule and surrounding limestone matrix. This specimen (also b. and b. below) has been etched and stained. The scale is in centimeters.



b. Massive, mottled chert with zone (z) between limestone and chert which is contiguous to interior areas of zone material.(arrow).



c. Mottled chert with interior areas of zone type material (circle).

FIG. 8. CHERTS WITH RIM ZONES AND RIM ZONE MATERIAL

TABLE 1

TABULATION OF CHERT SAMPLES: LOCATION, DISTRIBUTION, MEGASCOPIC DESCRIPTION

Chert Sample Zone Number	Location	Distribution[1,2]	Megascopic Description
34,35	Munnsville	Munnsville to Buffalo, in basal (Edgecliff Member) of Onondaga. More abundant in eastern part of state. In interval (5-10') above base of fm. in W. N.Y. 10-20' in Central, N.Y.	Characteristically mottled in color, medium and light bluish gray, light and dark gray. Commonly has bluish black outer zone of irregular thickness (1/4-3/4"). Resinous or waxy luster. No peripheral zone, but "zone-type" material distributed within chert. Occurs as nodular and compound nodular cherts outcropping along horizon. The nodules are evenly spaced (about 1'), not coalesced, and have a sharp contact with the matrix. They are 2 1/2-3" thick and 5-6" long. The chert in the lower portion of the member has the best developed typical characteristics. In the upper portion of the member smaller nodules may occur which are uniform in color and similar in properties to the light bluish gray component of the lowermost zones.
555	Buffalo	Buffalo to Leroy in upper half of formation. From approximately 100-120' above base of formation.	Essentially the same type as chert #45. Very light gray to yellowish gray, with brownish interior, very fossiliferous. 1-4" thick, 2-5" long, but some coalesced into stringers 53-54" long, spacing 1-3",
553	Buffalo	Buffalo to Leroy. Upper half of formation approximately 90 to 115 above base of formation	Brownish gray nodular chert with poorly developed peripheral zone contains a few fossil specs. Nodules 2-4" thick, 3-6" long, 1/2-1 1/2" apart, spacing 4-10".
43B - 1	Leroy	Buffalo to Phelps. Similar cherts occur in Buffalo section in interval	Dark brownish gray to medium dark gray, waxy, resinous luster, hairline cracks, smooth subconchoidal fracture. Peripheral

1) If thickness of interval in which chert occurs is given in feet, the figure is most reliable for the stratigraphic section from which the chert was collected, but is very approximate for adjacent sections.

2) Distributions more readily seen on correlation chart.

Chert Sample Zone Number	Location	Distribution	Megascopic Description
43B-1 (cont.)		between sample zones 57-B and 553.	zone may locally be well developed. Otherwise zone material is irregularly interspersed with chert and limestone. Occurs as elongated knobby stringers.
501	Phelps	Phelps area immediately above basal edgecliff.	Black to very dark gray, resinous luster, subconchoidal fracture, vertical hairline cracks. Thin peripheral zone may be present. Occurs in thin, persistent zones 3-4" thick, and 6-8" apart. Each 3-4" thick unit is composed of 2 to 3, one-half to 1" elongated chert bands. Rounded nodules are interspersed between the zones of long stringers.
42	Syracuse	Syracuse to Geneva, Moorehouse Member of formation. Lower part of upper half. In interval approx. 40-60' above base of formation.	Dark gray to grayish brown, resinous luster, fossiliferous, small hairline cracks. Sharp contact with matrix, peripheral zone absent or thin. Occurs in bands z93-6" thick) and 1-5' apart. Many are coalesced or almost coalesced to form continuous beds. There are some intervals of lensy inter-bedded chert and limestone.
57*	Buffalo	Uppermost zone of lower half of Onondaga formation, Buffalo to Batavia area. In interval approx. 50-75' above base of Fm.	Mottled light and light bluish gray to medium dark gray and dark bluish gray, but predominantly dark bluish gray. Dull resinous luster, subconchoidal fracture. Occurs in elongated seams of stringers with irregular top and bottom intermixed with limestone, shaly material, and stylolites.
57-A	Buffalo	Lower zone of upper half of formation. Buffalo area. May extend eastward since similar cherts and limestones are interbedded in the interval 43B-1 to 44A.	Medium dark gray to dark bluish gray, resinous luster; sharp subconchoidal fracture and occasional veins of milky white chalcedony. Occurs in elongated stringers with protuberences up and down. Interspersed smaller round nodules occur between stringers. Sharp contact with matrix, little zone material. Stringers are 1-2" thick, 15" long, 3-6" apart, and spaced about 1-4".

Chert Sample Zone Number	Location	Distribution	Megascopic Description
57-B*	Buffalo	Lower zone of upper half of formation, below 57-A. Apparently restricted to Buffalo area.	Mottled white, gray, to light brownish gray, blocky irregular fracture, dull luster, calcareous patches and vugs filled with drusy and crystalline quartz. Occurs in broad bands or beds (3-12" thick) which extend vertically up and down and enclose "islands" of limestone, but which also have a fairly strong alignment parallel to the bedding. The "beds" of chert generally have a sharp contact with the limestone, but within the areas of chert there are patches of limestone (usually partially silicified) having a diffuse gradational contact with the chert.
	Buffalo	Middle of upper half of formation, Buffalo area. Approx. 120-140' above base of formation.	Brownish gray with irregularly developed light brownish gray rim zone. Dull waxy luster. Occurs in discontinuous horizons of rounded nodules irregular in position. Nodules about 2" thick (lower part contains horizons of thicker (8") and longer (16") nodules spacing 1-2", horizons of nodules 6" - 2' apart.
38	Seneca Falls	Uppermost member (Seneca) Syracuse to Geneva. Comprises 1 to 5% of Seneca member. Approx. 60-80' above base of formation in east central area.	Dark brownish black to black, sharp contact with limestone matrix. Fossiliferous; no well developed peripheral zones; stylolites may define top and bottom of nodules and seams. Occurs in rounded nodules and thin stringer-like lenses.
45*	Batavia	Upper Onondaga, Leroy to Buffalo. Occurs in several horizons of nodules alternating with other cherts throughout the indicated stratigraphic interval. Approx. 90-115' above base of formation.	White or light gray to brownish gray, commonly with brownish interior. Poorly developed thin and discontinuous peripheral zone may be very light gray to yellowish gray. Sharp contact with limestone matrix. Dull, earthy luster, blocky fracture, many small very light gray fossil specks. Occurs in simple or compound rounded nodules 1-4" thick, 2-10" long, in horizons 3-24" apart. Spacing is variable, some horizons are coalesced to form seams.

Chert Sample Zone Number	Location	Distribution	Megascopic Description
44A	Leroy	Upper half of Onondaga formation Leroy to Buffalo. Occurs as bands in massive limestone, and as dispersed nodules. Approx. 75-90' above base of formation.	Dark gray to bluish gray, waxy luster, sharp fracture, no peripheral zone. Occurs in bands 2-3" thick 6" apart. The bands may not be completely coalesced in which case the appearance is of nodules outcropping along horizons.
44*	Leroy	Upper half of Onondaga formation Leroy to Buffalo. Approx. 60-70' above base of formation.	Brownish gray, waxy resinous luster, sharp fracture. Occasional thin or poorly developed peripheral zone. Sharp contact with limestone matrix. Occurs in persistent bands, 2-3" thick and 6-12" apart, which are elongated nodules. Smaller round nodules are dispersed between the more prominent chert bands.
73*	Avon	Moorehouse member. Upper half of formation. Canandaigua to Batavia. Distance to base of formation not known.	Mottled medium brownish gray to light gray with a light gray peripheral zone which is poorly developed. Irregular compound nodules, irregularly bedded; many are coalesced horizontally and vertically to form anastomosing network. Beds of chert about 3-4" apart, 2-4" thick, 18-24" long. Spacing is small and variable since most nodules are coalesced.
55 T.B.	Buffalo	Uppermost 8' of formation in Buffalo area.	White chert in massive limestone occurring 5' above Tioga bentonite. Essentially the same as #45 type chert.
45C and 45R	Batavia Area	Upper half of Onondaga formation Leroy to Buffalo.	Essentially the same as #44 except that the peripheral zone is well developed. 45C represents the chert and 45R the rim or peripheral zone which was separated from the chert and tested separately
42-3	Syracuse Area	Lowermost Onondaga from Munnsville to Buffalo	Essentially the same as Nos. 34 and 35.

*Primary Test Group

Explanation of Figure 9, "Stratigraphic Correlation and Sample Intervals"

In Figure 9 stratigraphic sections obtained in the field and from drill cores have been placed at the proper scale distance apart and lines indicating lithologic equivalence drawn between them. Solid lines represent contacts between intervals which are equivalent, or very nearly equivalent lithologically or which have similarities linking them together and distinguishing them from rocks immediately above or below. Dashed lines indicate questionable correlations and are used to imply that a particular interval may change in character laterally or may thin or wedge out laterally.

On the left side of each column a number corresponds with a sample interval indicated by a bracket (except for 55 T. B., which corresponds to the one chert to which it is adjacent). On the right side of each column some of the intervals are described briefly, but all intervals have been assigned a number, e.g. V-2, V-3a, etc., which corresponds to a detailed description to be found in Appendix A, since space on the chart does not permit fuller discussion.

The cherts in the columns are indicated by small, elongate, patterned, or clear shapes. The same pattern implies the same or very similar type of chert, but should not be interpreted literally for all intervals, because certain simplifications are necessary in indicating the cherts diagramatically. Detailed descriptions of the cherts are given in Table 1 and in Appendix A.

Where cherts occur in a banded or nodular fashion, the number of chert bands and their position is approximately correct to scale as in intervals V-1, V-2, II-1, I-1, etc., but their thickness is distorted. In other intervals it is not possible to do this and the cherts are indicated very diagramatically as in intervals I-5, II-9, II-15, etc.

The total percent of chert in the Onondaga formation generally increases from east to west, and the formation generally thickens from east to west.

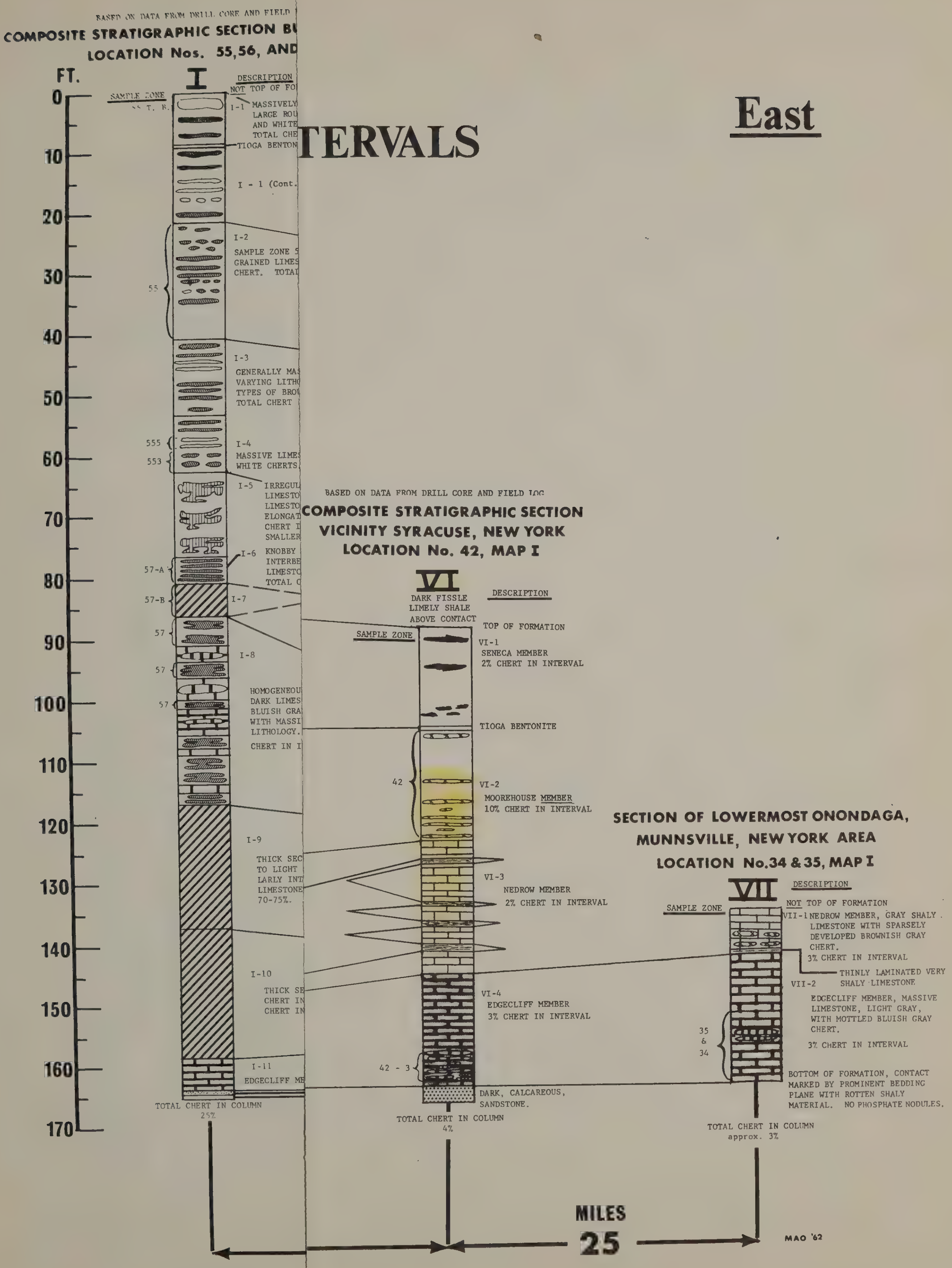
Only one lithofacies interval, or member, the Edgecliff, may be definitely stated to carry entirely across the state. The others either thin out laterally, or gradually change laterally, maintaining essentially the same thickness. It is not always possible to tell which is the case.

The same kind of chert will not occur in different types of limestone, but the same kind of limestone may sometimes carry different types of chert, e.g. interval I-1 (Figure 9). However, the Edgecliff lithology was not observed to carry any other but the #"35" type chert, and that type of chert was not observed in any other limestone lithology.

The members of the Onondaga formation (Edgecliff, Nedrow, Moorehouse, and Seneca) as defined by Oliver (21) are best developed in the central area of the state but change character to the west. The Nedrow member has been divided into two intertonging lithologies.

TERVALS

East



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STRATIGRAPHIC CORRELATION AND SAMPLE INTERVALS

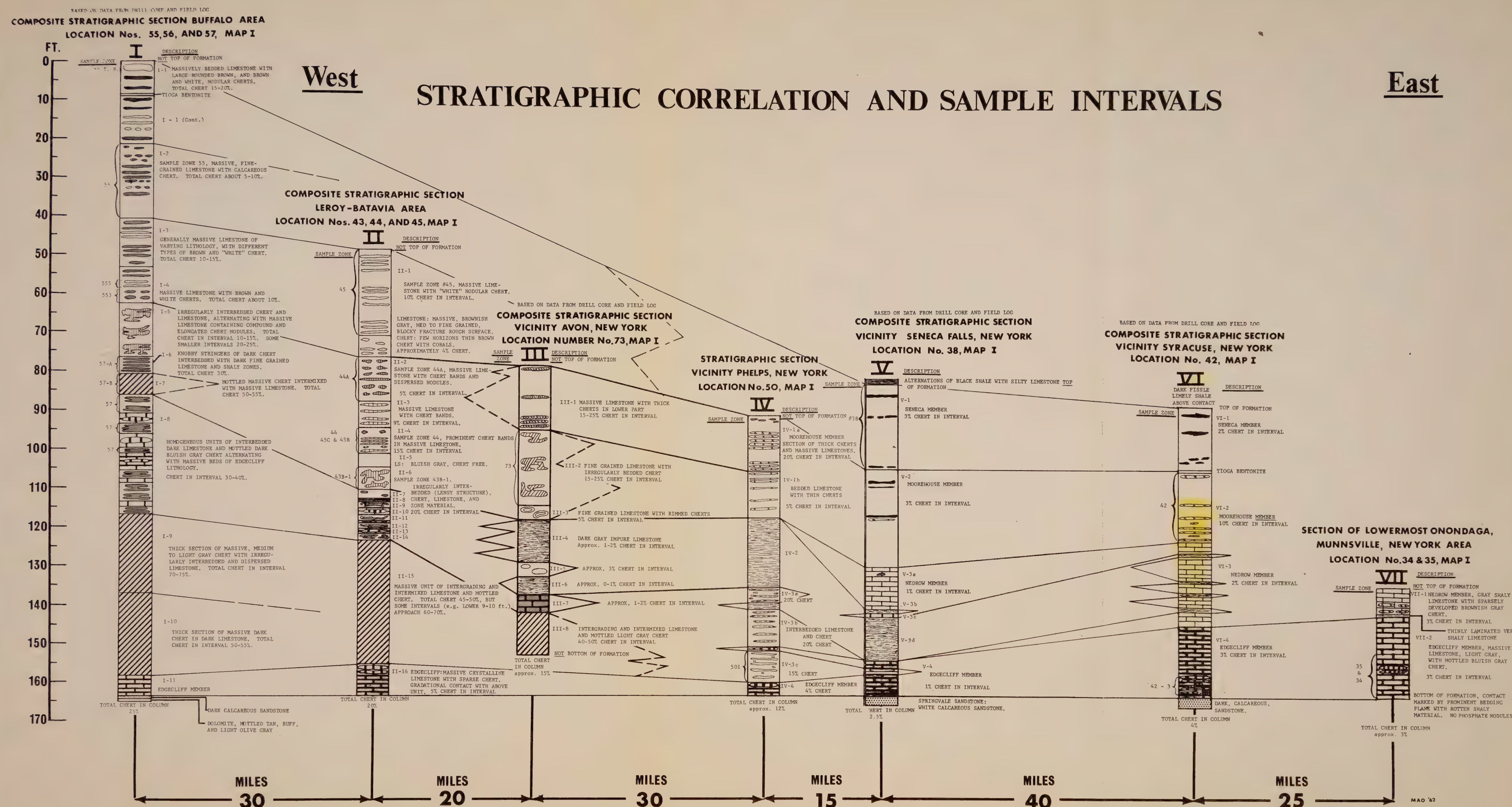


FIG. 9.

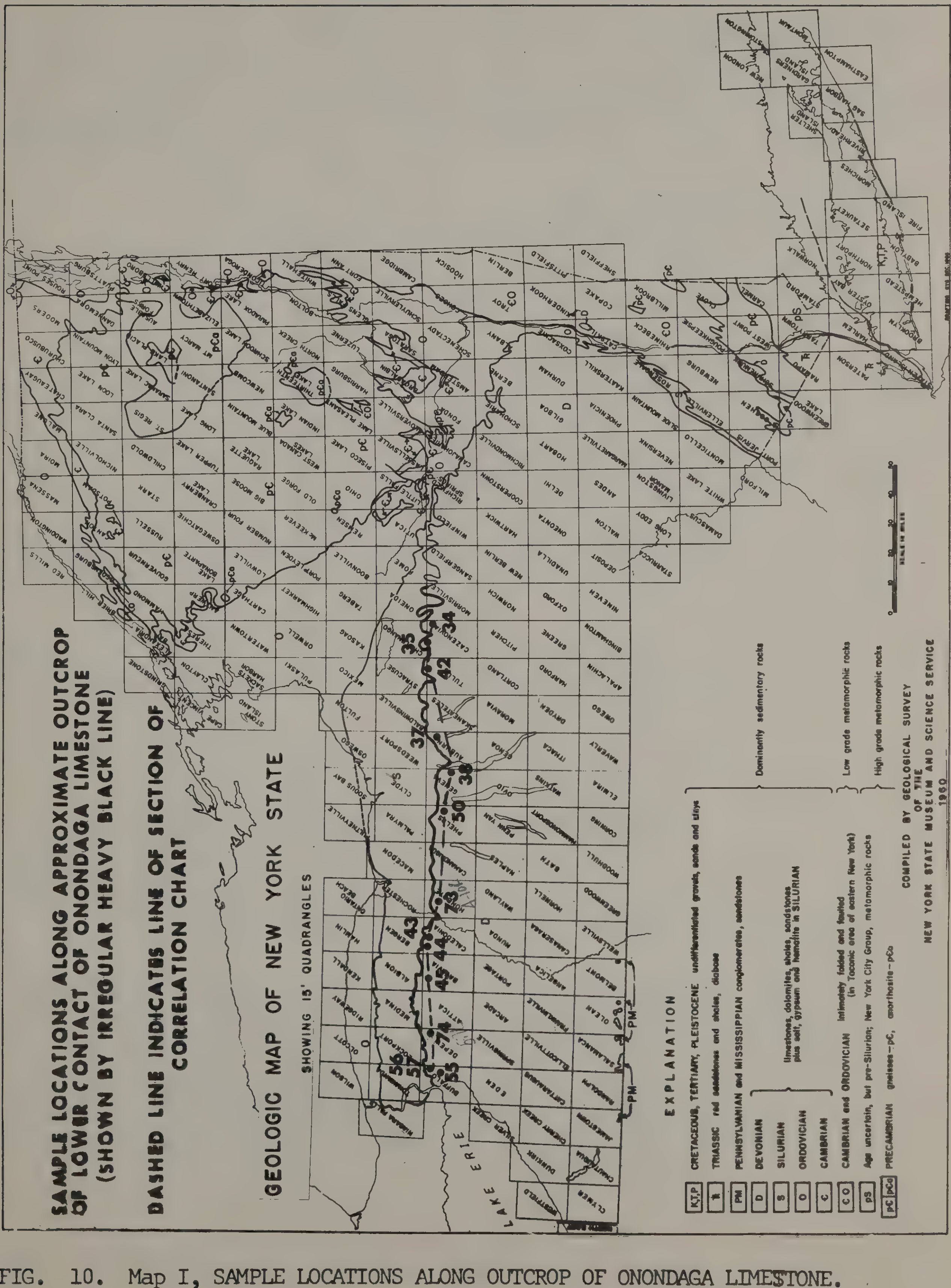


FIG. 10. Map I, SAMPLE LOCATIONS ALONG OUTCROP OF ONONDAGA LIMESTONE.

LABORATORY STUDIES

Petrographic Description of Cherts

Introductory Statement

The cherts of the Onondaga formation consist of combinations of silica and carbonate minerals in varying proportions. A catalogue of the terms describing the varieties of silica and carbonate minerals and accessories found in the cherts and employed in the descriptions and discussions is given below:

Silica Minerals and Mineraloids

(1) Cryptocrystalline quartz--very fine grained (less than about .001 to .002 mm) apparently equigranular aggregate. It may show very small, faint points of light under crossed polarizing prisms in the petrographic microscope. This indicates that there is some crystalline structure.

(2) Microcrystalline quartz--non-detrital quartz, aggregate of equant, anhedral, interlocking grains in random orientation. The grain size is about .005 mm. Under crossed nicols most grains show undulatory extinction, and the overall appearance is of closely spaced light gray to black spots. Where coarser grained and uniformly sized, the aggregate may appear as a fine grained, granular mosaic. A distinguishing feature of this material is that it does not show discrete grain outlines in reduced plane polarized light.

(3) Chalcedony--gives the appearance of being composed of fibers. It is found in three closely related but distinguishable modes of occurrence in the cherts.

(a) Spherulitic--rounded areas (where well developed) in which thin fibers are arranged radially. Under x-nicols (crossed polarizing prisms) a black cross remains stationary as the stage is rotated.

(b) Fibrous--thicker shorter fibers, marginally lining the outside of fossils or the inside of vugs.

(c) Flamboyant or plumose--composed of thicker, more indistinct fibers. Its appearance under x-nicols is somewhat like a flower with overlapping petals. This variety commonly predominates where the chalcedony occupies large sectors.

(4) Quartz

(a) Pseudoquartzite--coarser than microcrystalline. It consists of equant grains with slightly interlocking boundaries and has sharper extinction.

(b) Megaquartz--drusy quartz, geode quartz, authigenic quartz crystals. The grains are equant, usually bounded by plane or slightly curved surfaces. Extinction is sharp, and "mosaic" areas are common.

(5) Opal--isotropic, amorphous, high negative relief. This mineral is included for the sake of completeness. Certain isotropic forms of silica are apparently present in the cherts but it is not definitely known that they are opal.

Carbonate Minerals

(1) Calcite

(a) Anhedral, single fragments, with ragged edges, "floating" in the matrix of the chert.

(b) Microcrystalline dust--small pin points showing high relief, and high double refraction.

(c) Patches of partically replaced limestone intergrading with the chert groundmass.

(2) Dolomite (including ferrodolomite, ankerite, and related minerals)

(a) Coarse rhombs often imperfect--usually vein filling.

(b) Small sharp edged, well formed rhombic crystals--disseminated, ("floating")in the matrix of the chert.

Minor Accessories

(1) Pyrite

(2) Limonite

(3) Leucoxene (?)

(4) Sphalerite

(5) Detrital quartz

Abbreviations used in the Descriptions of the Cherts

The following abbreviations are used for the chert forming minerals listed above:

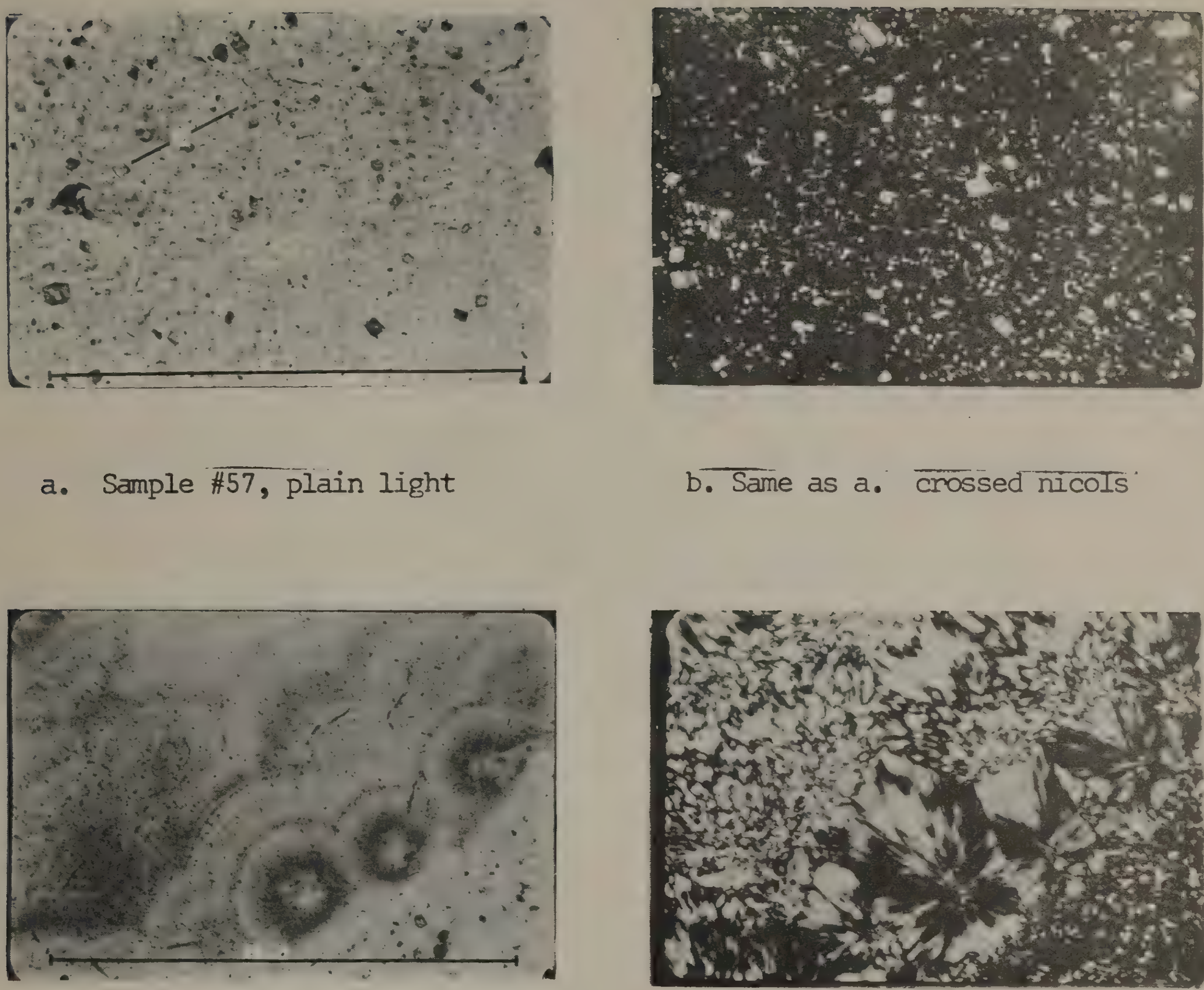
M--microcrystalline quartz.
K--cryptocrystalline quartz. May also include variations toward isotropic silica.
C--chalcedony, all varieties.
Q--pseudoquartzite and megaquartz.
O--opal, includes both isotropic silica and opaline material.
D--dolomite.
L--calcite, limestone.

Typically, Onondaga chert consists of a matrix or groundmass of microcrystalline quartz comprising from 75% to 85% of the chert. Within the groundmass are set dolomite rhombs and carbonate fragments. The K, C, Q, and O may appear to grade continuously into the groundmass or may be set apart from it by some line of demarcation visible either in plane light, reflected light, or x-nicols. Frequently, the occurrence of the above substances is related to obvious or ghost fossil shapes within the groundmass. The relative percentages of the silica minerals occurring within the cherts is apparently related to primary features of the limestone matrix among which are content and type of fossils, and grain size. There is a frequent association of a complex of chalcedony, cryptocrystalline quartz, and very dense cryptocrystalline quartz or isotropic silica, with replaced fossil shells. Clear, isotropic silica (probably not opal) occurs in small cracks and voids.

Size measurements of localized features and of individual grains were made by use of a micrometer eyepiece and reported wherever possible. In making size measurements, several areas of the slide are observed and the dimensions of the grains occurring under the scale of the eyepiece are recorded. The results are recorded (Appendix B) giving the arithmetic average of from 10 to 30 counts, and also the range between the smallest and largest grains counted. When grain size measurements are made of microcrystalline quartz, the sizes of various centers of maximum illumination are measured. These have diffuse boundaries and upon rotation of the stage are seen to grade by undulatory extinction into other adjacent small areas of maximum illumination. There are no true grains with definite visible boundaries under x-nicols.

Appendix B contains detailed petrographic descriptions of the six cherts for which mortar-bar tests have been completed. Note that each description is prefaced by an abbreviated description giving the approximate percentages of the various components of the chert.

The following Figures (Figs. 11 and 12) show microscopic textures of some Onondaga cherts.



a. Sample #57, plain light

b. Same as a. crossed nicols

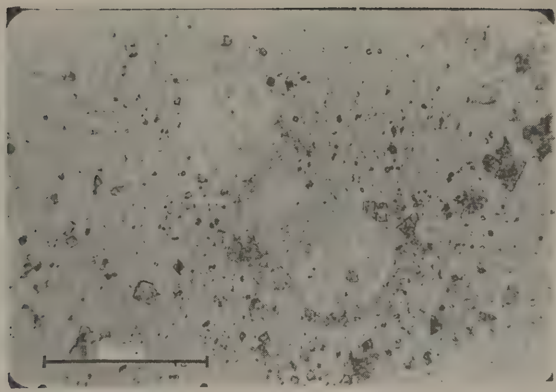
c. Sample #57, plain light

d. Same as c. crossed nicols

a. View of groundmass generally clear in plane polarized light, but with some cloudy or dusty areas. Note "floating" dolomite rhombs (D) which are distinguishable by their sharper outline. b. View of same area as in a. in crossed polarizing prisms, showing fairly uniform texture of somewhat finer than average grained microcrystalline quartz. The light colored rhombic areas are dolomite. The other small white or gray "pinpoints" are grains of microcrystalline quartz which are not extinguished in this orientation.

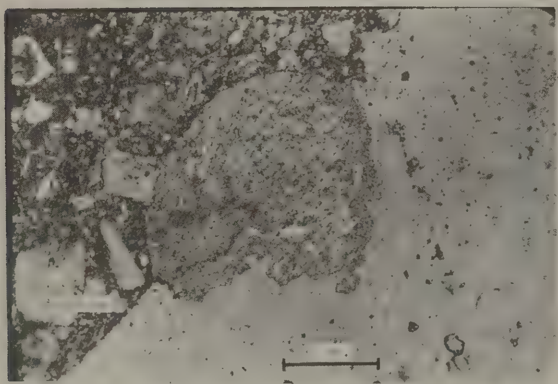
c. View of different area of same slide (used for a. and b. above) showing appearance of well developed rhythmically banded chalcedony in plane polarized light. In the lower right hand corner is a clear area of microcrystalline quartz which appears to grade into the larger area of chalcedony. d. Same slide under crossed polarizing prisms showing typical radial and plumose structure of chalcedony. Note area of microcrystalline quartz in lower right hand corner.

FIG. 11. PHOTOMICROGRAPHS OF CHERT THIN-SECTIONS.

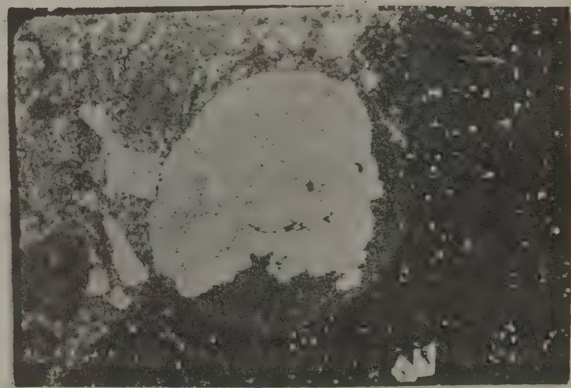


a. Sample #73, plain light

b. Same as a. crossed nicols



c. Sample #45, plain light



d. Same as c. crossed nicols

a. Fossil (crinoid) incompletely replaced by chert, in a matrix of microcrystalline to cryptocrystalline quartz. The groundmass is clear in plane light, with a few cloudy or dusty areas. Note sharply defined dolomite rhombs. b. In crossed nicols note the generally dark background caused by fine grain size. Larger, light colored, irregular or ragged patches (such as Ca) are composed mostly of calcite and are partially silicified limestone remnants.

c. Partially chertified fossil (prob. coral) across chert-limestone interface. Note abundant fossil debris in limestone. Chert is generally clear in plane light but has small areas of varying brightness and texture. d. Fossil in crossed nicols is in position of maximum illumination. The groundmass of the chert is generally fine grained (dark area). Note different texture in chert where fossil is replaced. Complete replacement of this fossil would ultimately produce an area of contrasting texture.

FIG. 12 PHOTOMICROGRAPHS OF CHERT THIN-SECTIONS continued.

Preparation of Samples for Testing

Bulk samples of chert were broken out of the limestone matrix by use of a standard hydraulic rock trimmer. Selected pieces representative of the most homogeneous and purest parts of the chert were then cleaned up by use of abrasive wheels to remove all adhering limestone. Zones of slightly different lithologic and chemical properties occurring between the chert and the limestone were generally discarded except in cases where this zone (the rim-zone) was needed for special tests.

Massive cherts frequently contain macroscopic islands or remnants of limestone; such cherts were broken down so that the smaller areas of limestone could be removed. Very small particles of limestone were not removed. They must be considered an integral part of the chert since all cherts in this study contain some calcite and dolomite on a microscopic scale.

Types of Tests

Cherts concentrated by the above method were used for the following tests: (after further processing appropriate for the particular test)

(1) Chemical analysis.

(2) X-ray diffraction.

(3) Specific gravity and absorption determinations.

 (a) Jolly balance method

 (b) Pycnometer method

(4) Quick chemical test.

(5) Mortar-bar expansion test.

Not all chert sample designations were used for all of the above tests. The following tabulation (Table 2) lists the sample designations of the cherts and the tests in which they were included (indicated by X). The location of a sample and its description may be found by reference to Figures 9 and 10, and Table 1.

The quick chemical and mortar-bar expansion tests require the use of different batches of samples from the same chert-type source. The control on items 1, 2, and 3 (above) was much closer since the same material which was used for Jolly balance determinations was powdered, mixed thoroughly and divided approximately in half. One half was used for chemical analysis, and the other for X-ray analysis and for pycnometer determinations of true specific gravity.

TABLE 2

TESTS TO WHICH CHERT SAMPLES WERE SUBJECTED

Chert Sample No.	Chemical Analysis	X-ray diffraction Analysis	Jolly Balance specific gravity & absorption	Pycnometer specific gravity	ASTM Quick Chem. Test	ASTM Mortar Bar Test	Petrographic Analysis
38	X	X	X	X	X	X in test	x
35	X	X	X	X	X	X "	X
57-A	X	X	X	X	X	X "	X
57-B	X	X	X	X	X	X	X
57	X	X	X	X	X	X	X
55	X	X	X	X	X	X	X
44	X	X	X	X	X	X	X
73	X	X	X	X	X	X	X
45C	X	X	X	X			X
45R	X	X	X	X			X
45	X	X	X	X	X	X	X
55T.B.		X	X	X			
34			X		X		X
42-3			X				
42					X		X
553					X		X
43B-1					X		X
44A					X		X
555					X		X
501					X		X
38b					X		X
Limestone Samples							
555					X		X
35					X		X
553					X		X

Chemical Analyses Of Cherts

Eleven chert samples were analyzed chemically, the results of which are reported in Table 3. The analytical procedures were adapted from ASTM C1845 and ASTM C114, the procedures for the analysis of silica refractory materials and portland cement respectively. The determinations were made by the New York State Department of Public Works, Albany, New York.

The method of selecting material and preparation of the samples for analysis has been described in the previous section. Note that: (1) Moisture is the small amount of water lost at low temperature (below about 105 C). (2) Loss on ignition (L O I) includes CO_2, SO_2, H_2O and organic matter. (3) MnO, and P_2O_5 were not separated from the Al_2O_3.

Discussion

As would be expected, the cherts studied consist dominantly of silica (from about 85 to 95%) - the second most abundant oxide is usually CaO, which is then followed by Fe_2O_3 and then MgO. Alumina is sometimes the fourth or fifth most abundant.

In addition to the four or five major components, there are small but very similar amounts in all the cherts of TiO_2, Na_2O, and K_2O.

The percent of CaO is inversely proportional to the percent SiO_2, as shown in Figure 13.

TABLE 3

RESULTS OF CHEMICAL ANALYSES OF CHERTS

	#57-A	#57-B	#57	#55	#44	#38	#73	#45C	#45R	#35	#45
Moisture	.16	.05	.11	.16	.15	.09	.12	.05	.05	.09	.14
L O I*	2.76	2.83	2.78	4.29	1.38	3.83	2.70	4.20	12.11	4.53	none
SiO_2	89.02	90.24	90.30	84.02	90.98	83.80	90.40	87.10	67.46	85.04	95.14
Al_2O_3**	1.17	.80	.66	1.33	1.14	1.17	.97	.88	1.13	1.35	1.01
Fe_2O_3	1.70	1.38	1.27	3.22	3.43	4.07	1.38	1.49	1.91	2.25	2.57
TiO_2	.11	.08	.09	.11	.15	.14	.09	.09	.12	.10	.12
CaO	3.02	3.95	3.64	5.87	1.57	5.65	2.57	4.09	14.83	5.25	.65
MgO	1.53	.81	.98	.98	.85	.80	.98	1.17	2.09	.80	.48
Na_2O	.14	.08	.15	.10	.14	.07	.17	.17	.12	.08	.08
K_2O	.34	.16	.24	.20	.31	.15	.17	.31	.22	.15	.17
	99.95	100.38	100.22	100.28	100.10	99.77	99.55	99.55	100.04	99.64	100.36

* Loss on Ignition includes CO_2, SO_2, H_2O plus organic matter.

** Includes MnO, P_2O5.

Note: Samples 45C and 45R are paired. Number 45R represents the rim zone, approximately 1/2" thick which surrounds 45C, the interior of the chert nodule proper.

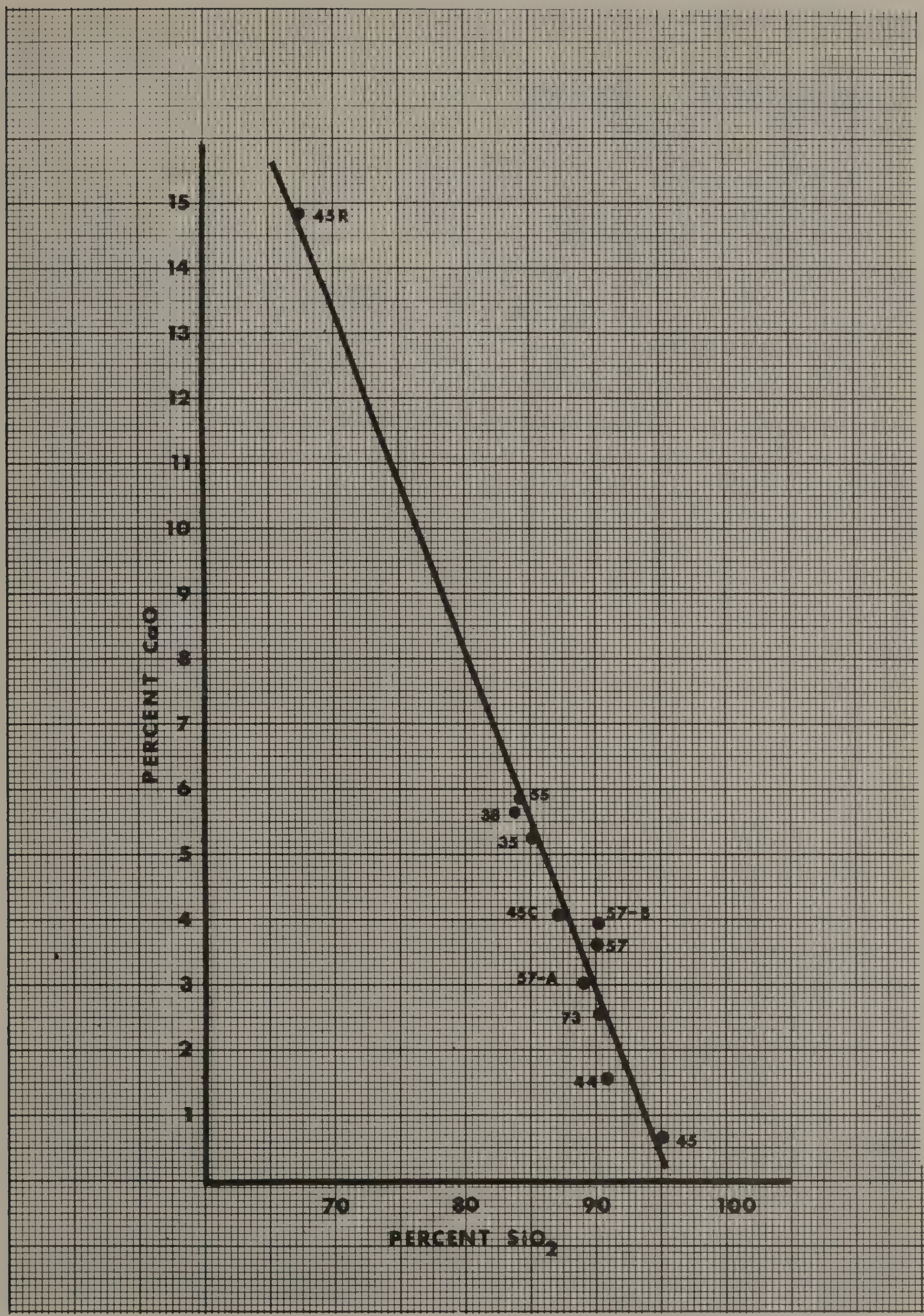


FIG. 13. PERCENT SILICA IS INVERSELY PROPORTIONAL TO PERCENT LIME IN CHEMICAL ANALYSES OF CHERTS.

X-ray Diffraction Analysis

An X-ray diffraction pattern for twelve cherts was obtained from the same powered material which was used for pycnometer determinations of specific gravity and for chemical analyses.

The diffractograms were obtained with a General Electric XRD-5 diffractometer[1]. Three quartz standards (1. Quartz rock crystal which was used for specific gravity standardization, 2. Permaquartz, the trade name for a variety of very pure novaculite supplied by the G. E. Company, 3. Novaculite from the R. P. I. mineral collection) were used for comparison with each other, for comparison with the ASTM data card for quartz[2], and for comparison with the diffractograms of the cherts. Excellent agreement was obtained in all the indicated comparisons.

The results of the X-ray determinations are given in Table 4. The relative abundance indicated for calcite and dolomite are based on comparisons of the heights of their principal peaks. Also indicated qualitatively is the strength of the principal calcite and dolomite peaks. A sharp narrow peak is considered strong, and a broader, more diffuse, usually lower peak is considered weak.

[1]Using CuK alpha radiation, 50 KV at 5 ma with Ni filter. Other data as follows: Beam Divergence was 3 Degrees, MR Soller Slit, 0.2 Degrees Collector Slit. Time Constant was 1.0 seconds with 5,000 counts/second. The scanning rate was 2 degrees of 2θ/minutes.

[2]Alpha-quartz would be more technically correct because x-ray analysis can distinguish between alpha-quartz (ordinary low temperature quartz) and beta-quartz ("high" quartz). Since virtually all quartz present in rocks at the earth's surface is alpha-quartz, the unqualified "quartz" is most commonly used and is understood to mean alpha-quartz.

TABLE 4

X-RAY DIFFRACTION RESULTS

Sample	Main Component	Second Component (Strength of Peak)	Third Component (Strength of Peak)	Comments	% Silica Chemical Analysis
45	Quartz			No dolomite or calcite peaks	95
73	Quartz	Calcite (medium)	Dolomite (medium)		90
44	Quartz	Dolomite (medium)		No calcite peaks	91
57	Quartz	Dolomite (strong)	Calcite (strong)		90
45C	Quartz	Dolomite (medium)	Calcite (medium)	Calcite and dolomite approx. equal quantity	87
38	Quartz	Calcite (strong)	Dolomite (weak)		84
35	Quartz	Calcite (medium)	Dolomite (medium)	Calcite and dolomite approx. equal quantity	85
45R	Quartz	Calcite (strong)	Dolomite (medium)		67
55	Quartz	Calcite (strong)	Dolomite (strong)		84
55TB	Quartz	Dolomite (strong)	Calcite (weak)		-
57-B	Quartz	Dolomite (medium)	Calcite (weak)	Calcite and dolomite peaks are low and about equal in height, indicating approximately equal quantities	90
57-A	Quartz	Dolomite (weak)	Calcite (weak)		89

Discussion

It is evident from Table 4 that the main component of all the cherts is quartz, and that either dolomite and/or calcite may be present in small amounts.

It cannot be stated with absolute certainty that there are no other silica minerals besides quartz in the cherts studied since the X-ray procedure used in this investigation will not produce a response to minerals present in amounts less than about 3 to 5%, and X-ray indentification of substances not possessing a regular internal structure is not possible. Also, as has been stated previously, petrographic examination reveals small areas of what has been described as cryptocrystalline-quartz or isotropic silica which may or may not be composed of quartz in a very finely divided state. If other silica minerals are present, the chief suspects would be opal (reported to give X-ray pattern of cristobalite), and keatite (12). No peaks could be indexed for these substances, but very small amounts could be missed in routine X-ray procedure.

Suggestive evidence for the idea that the silica component of the cherts is essentially all quartz is found in #45 which is 95% silica and which shows the clearest and sharpest quartz pattern, free of the peaks which in the other cherts are due to calcite and dolomite. Yet the microscopic appearance of 45 is variable with noticeable amounts of cryptocrystalline-quartz, chalcedony, and seemingly isotropic silica. The X-ray evidence suggests that regardless of what the microscopic texture may be, mineralogically the cherts consist essentially of quartz.

This finding has significance for the study of the reactivity of cherts in general, and for the Onondaga cherts in particular.

Previously, cherts considered to be potentially reactive have usually contained opal or chalcedony in quantities sufficient to be measured and described. Whether cherts which are composed essentially of the material known as microcrystalline quartz (as are the Onondaga cherts studied) are reactive or non-reactive has been uncertain. Some investigators have indicated that these types of chert are reactive (3,p4; 19,p25) others consider them non-reactive (13, 14). Part of the uncertainty stems from the fact that ordinary crystalline quartz is not definitely known to be deleteriously reactive (22, 18). Cherts not containing appreciable amounts of opal have been shown, usually by X-ray analysis, to consist mineralogically of quartz (the Onondaga cherts included) and yet, as stated above, there is evidence that cherts of this type may be deleteriously reactive. Further discussion of this subject, and a hypothesis to explain the reactivity of quartzose cherts is presented in Appendix C.

The results of this investigation support the latter viewpoint - that cherts composed essentially of (microcrystalline) quartz may be deleteriously reactive. This may or may not be found to be generally true, but it is a justifiable conclusion for the Onondaga cherts studied in this investigation. (The results of the quick-chemical and mortar-bar tests to estimate potential reactivity are presented in Table 6).

Specific Gravity and Water Absorption

Determinations of specific gravity and water absorption of fourteen cherts by the Jolly balance and (12 of the 14 by) pycnometer methods were undertaken to determine the relationships between those properties and the other characteristics associated with the deleterious behavior of the cherts.

By these methods information may be obtained on: true vs. apparent specific gravity[1], percent water absorption, and the deviation of apparent and true specific gravities from that which would be expected on the basis of mineralogical examination, X-ray, and chemical analysis.

Jolly Balance Method

The details of the Jolly balance method will not be given since they are available in any standard mineralogy text such as Dana's Manual of Mineralogy, (5). Briefly, the data for making the calculations are obtained by measuring the stretching of a spiral spring. A specimen is first weighed[2] in air and then weighed in water. The specific gravity is equal to the weight in air divided by the difference between the weight in air and the weight in water. For absorption measurements the procedure is modified slightly--two weighings in air are made, the first when the fragment is dry, and the second when the fragment is in a saturated-surface-dry condition after having been immersed in water for 24 hours.

The accuracy and reproducibility of the Jolly balance method was checked by test determinations on quartz (see Appendix D). Quartz was used because it can also serve as a standard against which to compare the specific gravities of the cherts, which, according to x-ray analyses consist essentially of quartz.

The following definitions of specific gravity and absorption are used in calculating the results that appear in Table 5[3].

[1] True specific gravity is the specific gravity of the pulverized material. It differs from the apparent specific gravity (see definition, page 36) in that it is the specific gravity of the solids excluding the impermeable pores or voids normal to the material. The extent to which the impermeable pores or voids are excluded depends on the size of the particles to which the material is pulverized. Thus, "true" and "apparent" specific gravity are relative terms. True specific gravity obtained by the pycnometer method is "truer" than that obtained by the Jolly balance method. In principle, a pure mineral such as quartz or dolomite has the same apparent and true specific gravities since it does not have any internal voids or pores.

[2] Since specific gravity is a ratio (wt. of substance/wt. of equal volume of water at 4 deg. C) the determination of absolute weights is unnecessary. A number which is directly proportional to the absolute weight is obtained in the Jolly balance method.

[3] Each value in Table 5 is the average of determinations on 9 individual pieces obtained by splitting a large homogeneous fragment.

Let: A equal the weight of oven-dry sample in air

B equal the weight of saturated surface-dry sample in air (after 24 hours immersion)

C equal the weight of saturated sample in water (after 24 hours immersion)

Then: $\frac{B-A}{A} \times 100$ equal percentage of absorption[1]

$\frac{A}{A-C}$ equal A.S.T.M. apparent Specific Gravity, i.e., the specific gravity of the solids including impermeable pores or voids not able to be saturated during the 24 hours immersion period.

$\frac{A}{B-C}$ equal A.S.T.M. Bulk Specific Gravity (dry basis) i.e., the average specific gravity of the entire rock including both solid material and voids.

Specific Gravities by Pycnometer[2] Method

For the determination of specific gravities by the pycnometer method, the material is first reduced to a powder of the desired size by crushing and grinding. The crushed material is then ground in a micro-mortar and sieved to pass a number 200 screen. Particles passing this screen have a maximum size of about .074 mm (74 microns). The quartz powders thus obtained were used directly for pycnometer determinations. The chert powders were mixed thoroughly and divided in half; one half was used for chemical analysis and the other half for X-ray analysis and for pycnometer determinations.

The pycnometer method is given in Appendix D. The accuracy and reproducibility of the pycnometer technique as used in this investigation was tested by determinations on two sizes of crushed quartz crystal.

The values for the specific gravity of quartz obtained by the three methods of determination: 1. Jolly balance, 2. Pycnometer using coarsely crushed crystal, (see Appendix D), 3. Pycnometer using powdered crystal - agree with the values for this mineral reported in standard references. The value of 2.65 is usually found in mineralogy texts such as Dana (5) or Berry and Mason (1). The Handbook of Physical Constants (11) gives a value of 2.654. Thus it may be concluded that the accuracy and reproducibility of the methods used are adequate for their intended purpose.

The results of the apparent specific gravity, absorption, and true specific gravity determinations are presented in Table 5.

[1]For those samples which do not show any absorption, apparent specific gravity is equal to bulk specific gravity since, in that case, B and A would be equal.

[2]A pycnometer is a small bottle with an accurately determined volume. The specific gravity of a powdered substance is determined by a sequence of weighings in which the pycnometer is weighed: (1) empty, (2) with powdered substance, (3) with powder plus enough water to fill it, and (4) filled with water alone.

TABLE 5

APPARENT, BULK, & TRUE SPECIFIC GRAVITY AND ABSORPTION OF CHERTS

Sample	ASTM Apparent	ASTM Bulk Dry Basis	"True" Pycnometer s.g.	Percent Absorption
Quartz Crystal	2.655		2.648	
57-B	2.64	2.58	2.629	.85
73	2.61		2.603	none
44	2.59		2.603	none
57	2.60		2.638	none
55	2.62		2.604	none
45	2.57	2.34	2.604	3.89
45R	2.63		2.642	none
45C	2.60		2.618	none
35	2.60	2.59	2.602	.10
38	2.58	2.55	2.627	.23
57-A	2.61	2.60	2.591	.07
55-T	2.63	2.47	2.621	2.36
34	2.63	2.59		.59
42-3	2.62	2.60		.30

Discussion

Samples 35, 34, and 42-3 are the same chert type from the same lithologic-stratigraphic interval in different locations separated by about 15 miles. It is evident by comparing their apparent and dry specific gravities (Table 5) that the same chert type may exhibit similar but not necessarily the same specific gravity. Note that the three samples of this chert all show a small percentage of absorption (approx. .1 - .6%), and have qualitatively maintained this property in common. Samples 45 and 55-T also are the same chert type, but from different stratigraphic intervals in different quarries. Their specific gravities are rather different, but again, both exhibit comparable percent absorptions.

Examination of the results also shows that all the samples have apparent specific gravities less than quartz (2.65). The presence of calcite and dolomite (s.g. 2.72, and 2.85 respectively), which occur to a greater or lesser extent in all the samples, has not raised the specific gravity above the value (2.65) where there would be uncertainty as to the relative proportions of quartz, dolomite, and calcite present.

Furthermore, the determination of the true specific gravity (by the pycnometer method) has not resulted in increases which approach the value for quartz. The values, for the silica fraction, may be regarded as appreciably lower, again because of the presence of the heavier minerals, calcite and dolomite. The only sample close to quartz in true specific gravity is 45R. This is peripheral zone material, surrounding the No. 45C chert nodule, which is richer in CaO and MgO (hence in calcite and dolomite) than any of the other cherts.

In principle (except for pure minerals such as quartz, calcite, etc.) the specific gravity of a material should increase from Jolly balance to pycnometer, assuming there is porosity or void space present above the 74 micron size--the maximum size of material passing the 200 mesh sieve. This increase is observed for seven of the twelve cherts tested by both methods; the other five show decreases in specific gravity, from Jolly balance to pycnometer, of roughly about the same order (.007) as the decrease observed for the pure quartz crystal (Appendix D). Perhaps the decrease is partially due to the effect discussed in Appendix D. At any rate, since both cherts and quartz were processed and tested in exactly the same manner the results may be compared.

The cherts being less dense than quartz may be due to two situations:

(1) The silica component of the chert is not quartz, but some less dense form of silica. (e.g. opal, tridymite, cristobalite)

or

(2) The silica component of the chert is quartz but is combined with some less dense material such as air or water.

The first alternative would seem to be ruled out by the result of the X-ray determinations and the petrographic analysis from which it was deduced that the silica component of the chert is essentially composed of quartz. The specific gravity determinations show that the cherts are significantly lighter than they

should be if they were composed of quartz, and suggest that alternative (2) is the correct interpretation. That is, the cherts consist of a quartz framework with a large number of micropores which exert a buoyant force and depress the specific gravity.

It has been shown previously, in the section on chemical analysis, that the percent of silica in the cherts studied is inversely proportional to the percent CaO. All other things being equal, the apparent and true specific gravities of the cherts might be expected to show some relationship to their chemical composition. That is, if the silica fraction in each chert had essentially the same specific gravity then the specific gravity of the chert should be directly proportional to the carbonate content, or inversely proportional to the silica content.

A plot of apparent and true specific gravities vs. percent CaO is presented in Figure 14. Four samples (45, 44, 73, and 57-B) show a direct relationship between apparent specific gravity and percent CaO. However, the position of the other points indicates that additional variables are operating and that specific gravity must still be considered largely independent of percent CaO. The evidence suggests that the specific gravity of the chert is chiefly a function of some property of the state of aggregation of the silica and its lighter constituent. Thus, specific gravity may be related to variations of petrographic character within the silica. A simple and sensible assumption to make is that the different chert forming minerals M, K, C, and O, and their textural variations, hold different varying percentages of micropore space (and/or water).

This association of the silica and its lighter constituent is very intimate and must be considered, as it is by most investigators, an intrinsic property of the material. Small bubbles of water and/or air have been reported as occurring in silica minerals of this type (6, 16, 22), and some workers contend that all the properties of these "subcrystalline" silica materials can be attributed to their consisting of extremely fine-grained crystalline quartz in combination with varying amounts of water and bubbles. If this is true, then the demonstrated chemical reactivity of the quartzose cherts studied in this investigation is an irregular effect which should not occur, since normal crystalline quartz is not known to be deleteriously reactive.

A hypothesis to reconcile this irregularity is presented in Appendix C.

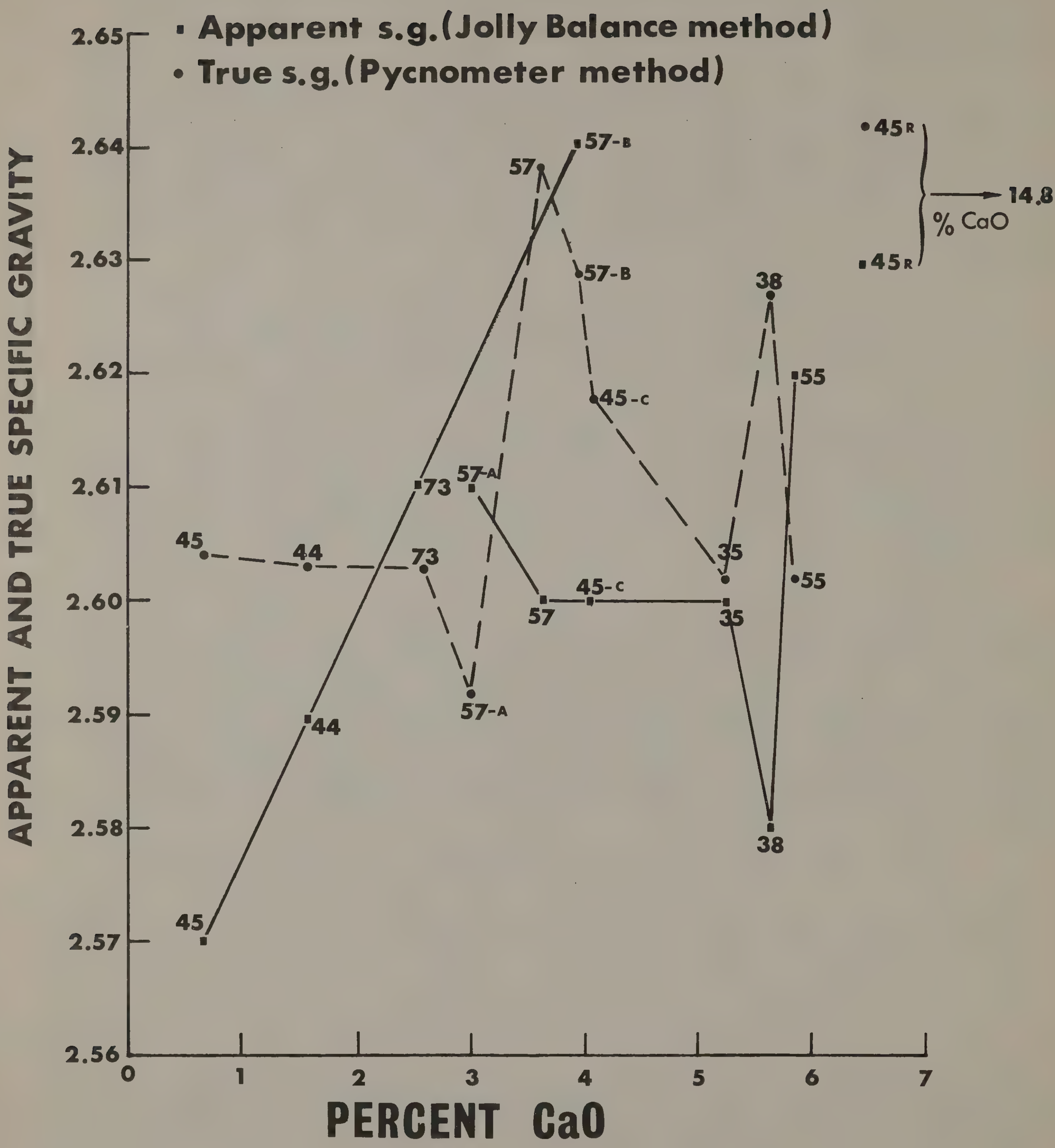


FIG. 14. NEITHER APPARENT NOR TRUE SPECIFIC GRAVITY OF CHERTS IS SYSTEMATICALLY RELATED TO PERCENT LIME OR SILICA.

Quick Chemical Tests

Seventeen chert samples and three limestone samples were tested by the quick chemical method (A.S.T.M. Designation C 289 - 57 T). The results indicate that all of the chert samples would be classed as deleterious and all three limestone samples innocuous according to the standard interpretation. The results of the tests are presented in tabular form in Table 6 and in graphic form in Figures 15 and 31.

The results of the quick chemical tests run in this investigation, when compared with the results of the mortar-bar expansion tests (presented in the next section), are relatively free of the complicating factors or conflicting interpretations which have often been reported by previous investigators. The "carbonate effect" caused no serious interference, and the agreement between quick chemical and mortar-bar results was good except in one case. Of the six cherts tested by both methods, those indicated to be deleterious in the mortar-bar expansion were also deleterious in the quick chemical test. One sample (No. 45) was deleterious in the quick chemical test but did not exceed .1% expansion[1] in the mortar-bar test. Possible reasons for this are presented in DISCUSSION OF RESULTS.

The quick chemical test is a method for determining the potential alkali reactivity of aggregates and for estimating their capacity to produce expansion when used with high alkali cement.

The potential reactivity of an aggregate is measured by the amount of silica dissolved (quantity Sc) by a 1N sodium hydroxide solution from a sample crushed to the No. 50 to No. 100 size and the concomitant reduction in alkalinity (Quantity Rc) of the solution.

[1]The suggested A.S.T.M. limit for distinguishing deleterious from non-deleterious aggregates. A.S.T.M. designation C33 - 55T.

TABLE 6

QUICK CHEMICAL AND MORTAR-BAR
TEST RESULTS IN ORDER OF INCREASING Sc/Rc

Sample Identification	Alkalinity Reduction (Rc)	Dissolved Silica (Sc)	Ratio Sc/Rc	% Expansion Mortar-Bar (orig. lg.=10")	Pessimum Proportion
555 (ls.)	165	21	.127		
35 (ls.)	68	12	.176		
553 (ls.)	161	99	.615		
42	96	205	2.14		
35*	111	270	2.43		
553	105	259	2.57		
38*	92	241	2.62		
55	111	312	2.81	.105	50%
45	174	504	2.90	.055	10%
43B-1	101	322	3.19		
57-A*	124	401	3.23		
44	95	312	3.28	.215	50%
73	106	353	3.33	.190	50%
57-B	141	482	3.42	.200	20%
44A	84	314	3.74		
57	90	347	3.86	.225	50%
555	130	508	3.91		
501	69	272	3.94		
34	75	323	4.31		
38b	60	296	4.93		
Q (rose quartz)	41.8	21.4	.51		

*Presently in mortar-bar test (August 1962)

When the test was devised, a large number of substances were tested both by the mortar-bar method and by the (then experimental) quick chemical test. After the results of the quick chemical test were plotted (S_c and R_c), it was found that a line could be drawn separating points representing aggregates causing more than .1% expansion in a year on the mortar-bar test from points representing aggregates causing less than .1% expansion in a year. The locus of the line approximates the ratio $S_c/R_c = 1$. Deleterious materials usually have a value greater than one, innocuous materials less than one. Other aggregates can be identified as reactive or innocuous by subjecting them to the quick chemical test, and plotting the results on a diagram such as Figure 15, using the same line of demarcation.

The ratio S_c/R_c expresses the rate of dissolution of silica per unit reduction in alkalinity of the NaOH solution. It is therefore a measure of the efficiency with which a particular type of aggregate will utilize the available alkalies in order to produce a given amount of silica, e.g., those aggregates releasing a large amount of silica but causing only a slight reduction in alkalinity use the available alkalies very efficiently.

The ratio S_cR_c is, therefore, an index to the deleterious or innocuous character of an aggregate; however the magnitudes of S_c and R_c individually are necessary for a full interpretation. Obviously, points located in widely separated parts of the deleterious field can have the same S_c/R_c ratio. In the present study the magnitude of the ratio was found to agree fairly well with the magnitude of the mortar-bar expansion. (See section DISCUSSION of RESULTS).

Each particular area of the quick chemical test graph has a certain significance (17).

Points in the upper left corner represent materials which release little silica but reduce alkalinity greatly. They are unstable, but the instability favors their non-deleterious character. Points in the lower left are comparatively stable, yet release small amounts of silica at moderately efficient rates, i.e., they do not cause a large reduction in alkalinity. Points in the lower right release large amounts of silica, but cause a comparatively small reduction in the alkalinity. Materials in this area (below about 100 to 110 R_c and above about 200 S_c) are theoretically very dangerous. They utilize the alkalies efficiently, thus alkaline solutions persist, and the reactions are long-continued. Twelve of the 17 cherts tested fall into this area of the quick chemical plot. Points in the upper right are least stable. They release large quantities of silica but cause correspondingly high reductions in alkalinity. Four cherts tested fall into this area of the quick chemical plot. (Samples 45, 57A, 57B, and 555).

Which of the two reactive areas, upper right or lower right, contains the materials producing the most expansion is a question not yet answerable, if indeed magnitude of expansion is related in some way to position in these areas. The data obtained in this study (limited in comparison to some of the larger, long term studies which have been made) suggest that cherts of a comparable S_c/R_c ratio will produce comparable expansions, but that cherts in the upper right area of the graph will have lower pessimum proportions. (See page 50 for definition of pessimum proportion).

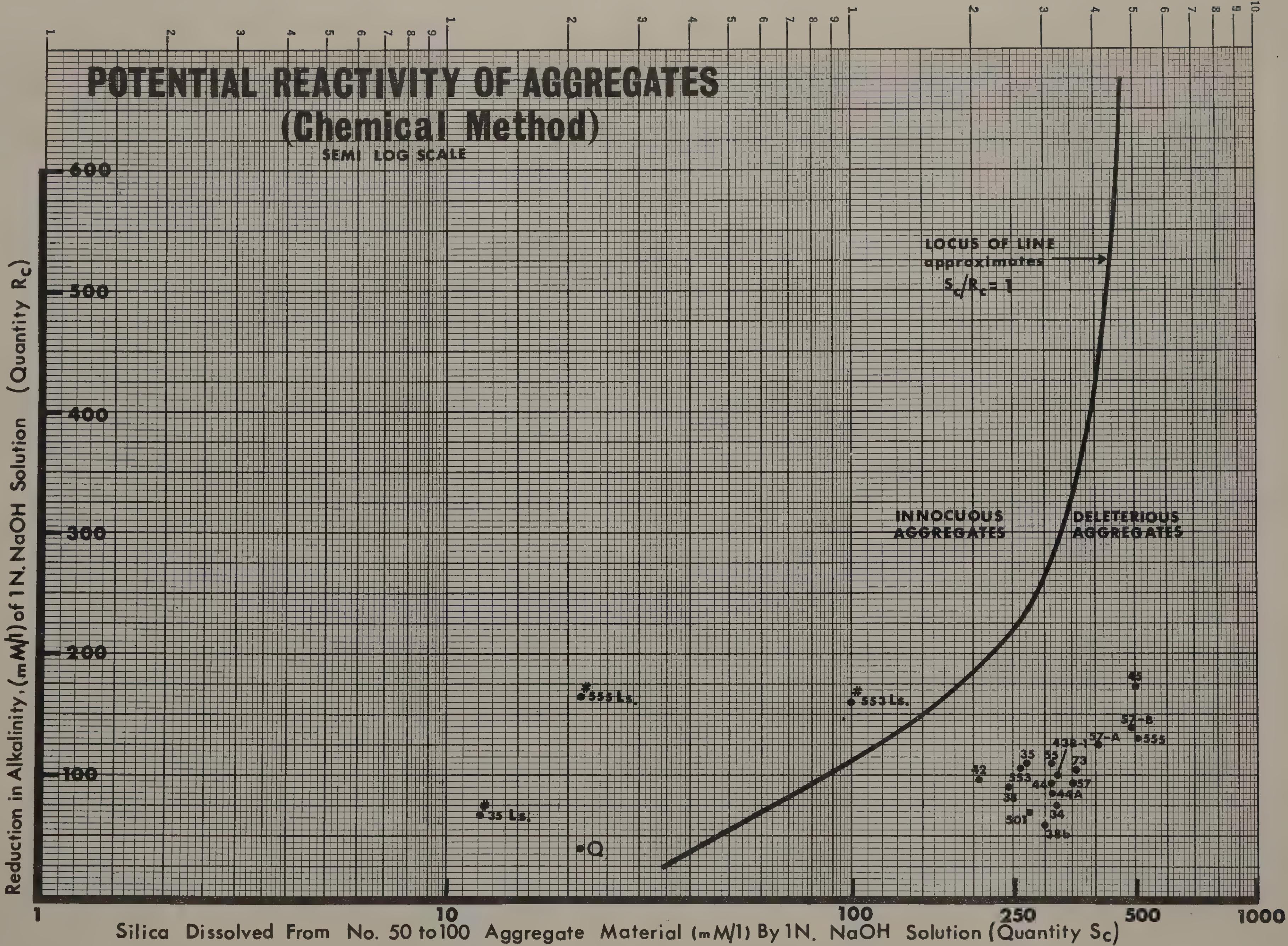


FIG. 15. RESULTS OF QUICK CHEMICAL TESTS.

Mielenz (17) deduced that the pessimum proportion should be low for those materials which cause a large reduction in alkalinity (R_c) and it should be higher for those materials which cause a smaller reduction in alkalinity. This relationship is consistent with results of the present study. Although not explained by Mielenz, the relationship probably exists because materials causing a high reduction in alkalinity will deplete whatever alkalies are available in the mortar-bars rather quickly, and surpass the point where expansion is directly proportional to concentration. Therefore, whatever expanding occurs must take place at a low concentration of reactive material.

In the graph (Figure 16) following Table 7, below, the relationship between the mortar-bar pessimum proportion and the reduction in alkalinity on the quick chemical test is shown for the six cherts tested by both methods. A good correlation between these two factors is indicated here. More precise location of the pessimum proportion by use of smaller increments of percent chert in the mortar-bar test, (the percentages used were 5, 10, 20, 50, 75, and 100% chert) would probably have improved the distribution of the points in the 50% P_p cluster.

TABLE 7

REDUCTION IN ALKALINITY IS INVERSELY RELATED TO PESSIMUM PROPORTION

Sample Number	R_c	Pessimum Proportion
45	174	10%
57-B	141	20%
55	111	50%
73	106	50%
44	95	50%
57	90	50%

The above information is presented in the following figure in graphic form.

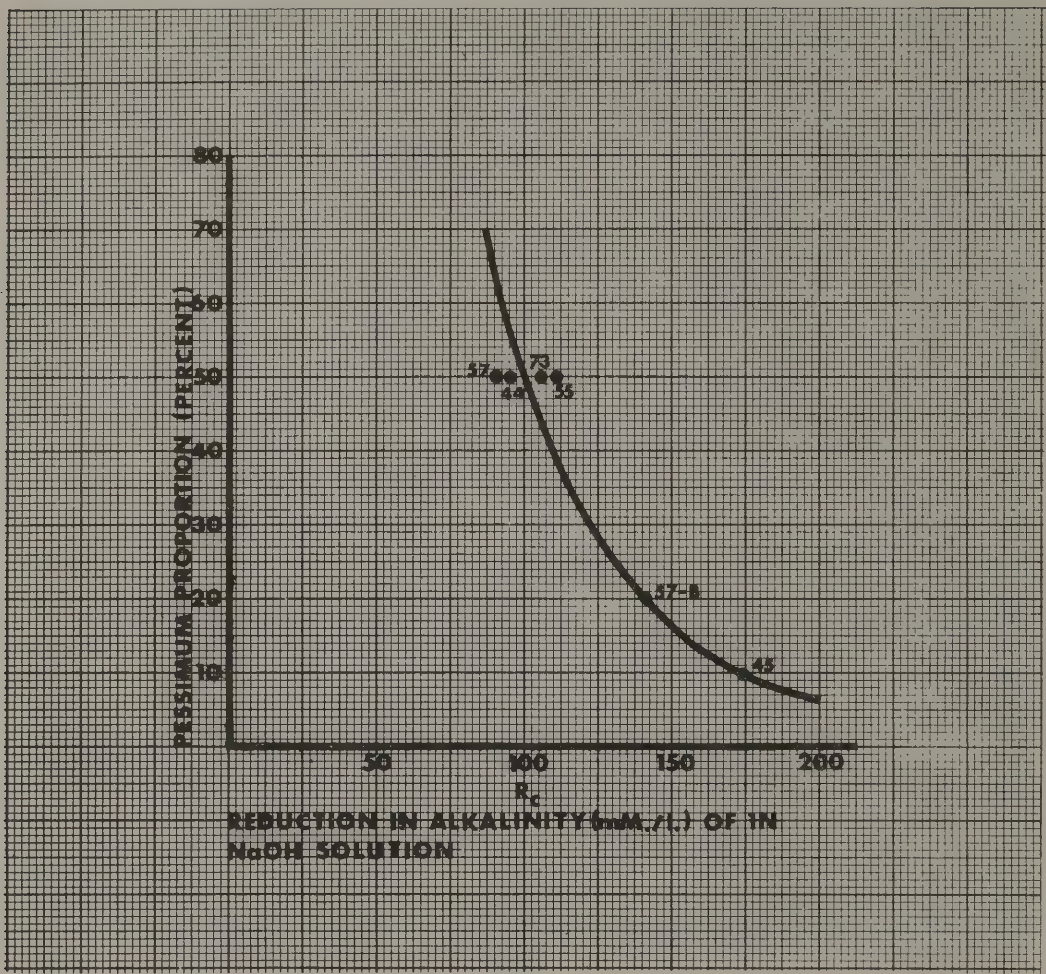


FIG. 16. REDUCTION IN ALKALINITY IS INVERSELY RELATED TO PESSIMUM PROPORTION

The "Carbonate Effect" on the Quick Chemical Test

Substances such as dolomite (including ferroan dolomite, magnesite, and siderite) have been shown to produce an irregular increase in the reduction of alkalinity (R_c) and decrease in the concentration of silica. (2, 17, 20) The result of such interference would be to shift data points in the deleterious area of the field upward and to the left (see Figure 15) where they might then be located in the innocuous area of the field.

Although all of the cherts contain the minerals calcite and dolomite as established by petrographic examination, X-ray[1] and chemical analysis, those minerals have not influenced the results of the tests to the extent of causing any chert to be classed as innocuous. A more complete discussion of the carbonate effect with respect to increased R_c and depressed S_c may be found in Appendix E.

Reproducibility of the Same Type of Chert on the Quick Chemical Test

Comparison of the quick chemical test results of the three pairs of samples Nos. 38 and 38b; 34 and 35; and 555 and 45 indicates that variable results may be obtained from samples which were intended to be the same material within the limits of the term "sample designation." For purposes of clarity, the points under discussion have been drawn alone on Figure 17 . Note that this is still a semi- log scale. Also refer to Figure 31 in which the information is plotted on a linear scale.

Some discussion of what is meant by the "sameness" of the material is in order. Samples 38 and 38b are the same chert type from the same lithologic-stratigraphic interval in the same quarry; in other words, duplicate samples drawn from stock supplies of that material. They are not a split sample of the same powder prepared for the test.

Samples 34 and 35 are the same chert type from the same lithologic-stratigraphic interval in different quarries about 12 miles apart. This chert is very distinctive and occurs in a restricted interval in the two locations.

Samples 45 and 555 are the same, or at least very similar, cherts from the same lithologic-stratigraphic interval in different quarries about 32 miles apart. This chert is also very distinctive, but occurs in a somewhat thicker interval and in several zones alternating with other types of chert within that interval.

[1]No. 45 did not show any calcite or dolomite on the X-ray diffraction pattern but did show (lower than average amounts of) CaO and MgO in chemical analysis, and the minerals calcite and dolomite in thin-section, and on stained study slabs.

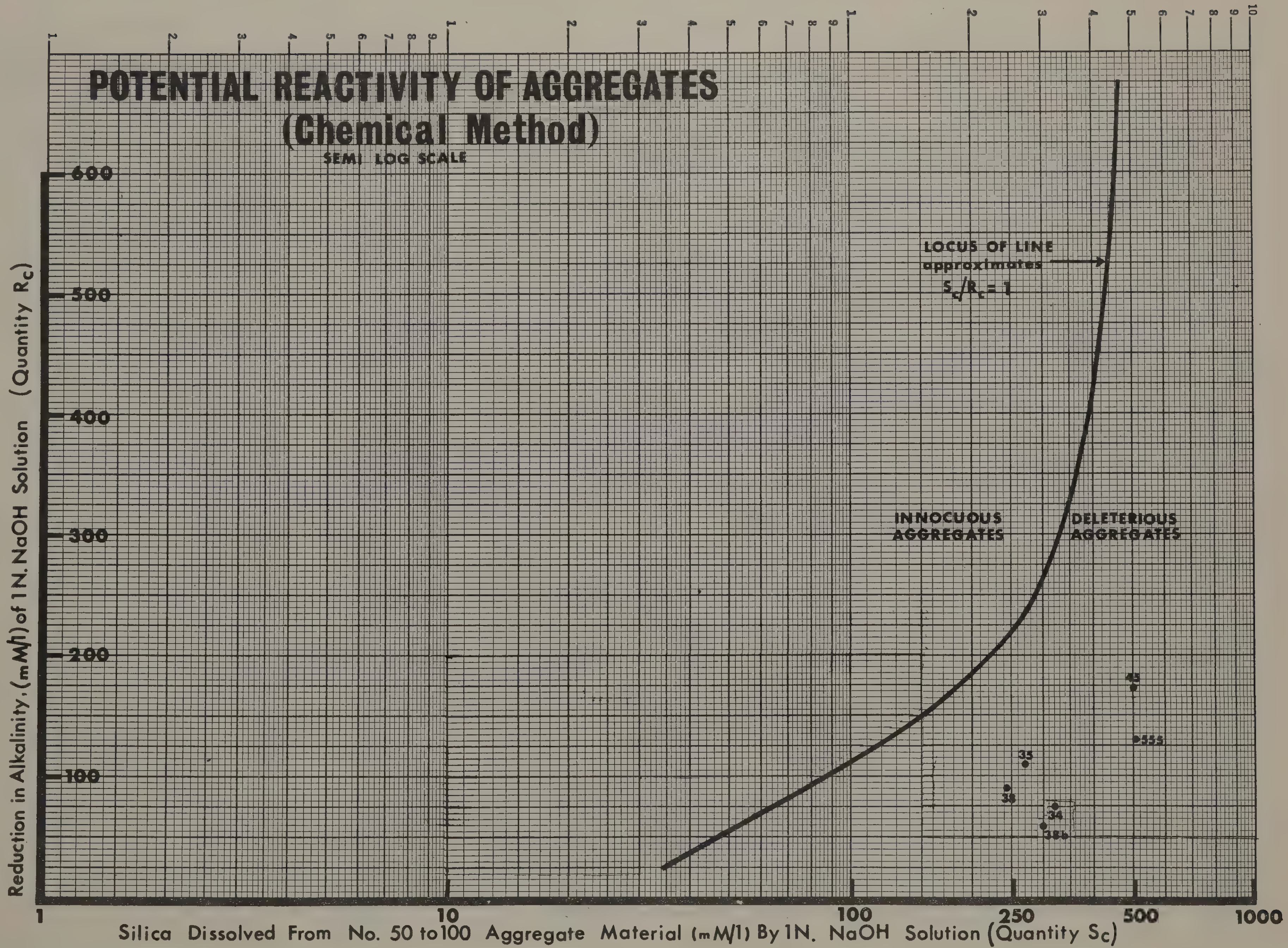


FIG. 17. REPRODUCIBILITY OF SAME TYPE CHERTS ON QUICK CHEMICAL TEST.

Geologic units may maintain essentially the same chemical character over many miles but if there is any difference in the chemical character between the members of the three pairs of samples it is judged more likely to be between 45 and 555, 34 and 35, and 38 and 38b in that order.

The reproducibility shown in Figure 17 is judged to be fair in that 34 and 38b tested close to their mates 35 and 38 respectively. However, these four points are all in the same general area of the graph. Number 45, however, is located in a different area of the graph and significantly its mate (555) tested close to it.

The reason for the lack of very close or exact reproducibility between the samples is not known, but neither is it known what degree of reproducibility is desirable or intolerable. The discrepancies shown in Figure 17 may be within the limits of error of the entire procedure--considering both chemical determinations and geologic variability.

Since exact duplicate or "split" samples were not run in the present series of tests for either the Quick Chemical Test of the chemical analysis, it is not possible to draw conclusions regarding reproducibility of chert samples which had the same chemical analysis. It is evident, however, that chert samples which would be described geologically as the same may give (slightly) different quick chemical test results.

This problem of reproducibility has been examined by Mielenz (20) and others (2). Mielenz has proposed certain modifications of the quick chemical test to improve reproducibility and to remove irregular effects caused by the presence of magnesian carbonates and hydrous silicates (the carbonate effect). These effects, as discussed elsewhere, were not considered to be a problem in the present investigation.

Mortar-bar Tests

In the mortar-bar "Method of Test for Potential Alkali Reactivity of Cement-Aggregate Combinations" (ASTM Designation C227) the aggregate is combined with cement in a specified grading, fabricated into mortar-bars 1 x 1 x 10", and stored over water in covered containers at 100 deg. F. The length of the bars is measured periodically. The expansion attained by the mortar-bars indicates the potential alkali-reactivity of the cement-aggregate combination. Mortar-bars exceeding 0.1% expansion within 12 months are considered to be excessively expansive.

In principle, method C 227 is a test of a "cement-aggregate" combination rather than a test of an aggregate. It is standard operating procedure, however, to apply the test as an evaluation of the potential reactivity of an aggregate. In this case, a standard high-alkali cement (greater than .6% total alkalies) and a standard grading is used so as to remove these factors as variables (19).

Cherts Tested by the Mortar-bar Method

The results of mortar-bar tests, performed according to ASTM C 227, on six cherts (Samples 55, 45, 44, 73, 57-B, and 57) are included in this report (Table 6). The cement used for fabricating the mortar-bars was a Type I, general purpose cement of .89% alkalies (total Na_2O and K_2O) as determined by the New York State Department of Public Works[1]. The six cherts were combined in six concentrations (5, 10, 20, 50, 75, and 100% of the total aggregate) with rose quartz. The testing of varying concentrations of chert is standard procedure because it is anticipated that not all concentrations of chert will be equally expansive. The reason for this is discussed below.

The Pessimum Proportion

Stanton, in early studies of the reactivity of siliceous substances with alkalies, found that the amount of expansion increased with the concentration of reactive material to a certain point, after which expansion decreased with increased concentration of reactive material. Pessimum proportion is a term used by T. E. Stanton to designate the proportion of reactive constituent in an aggregate at which maximum mortar expansion occurs.

Pessimum proportions have been reported from less than 5% to 100% reactive material[2].

The phenomenon of the pessimum proportion is quite evident when studying the results of a series of mortar-bar tests in which the reactive constituent has been blended with a control aggregate in varying proportions - as has been done in the present investigation.

Mielenz (17) suggests that the phenomenon of the pessimum proportion represents "the operation of two opposing characteristics of cement aggregate reaction, namely: the tendency for increased expansion of the mortar as progressively more reactive particles are made available for attack; and the tendency

[1] A chemical analysis of the cement is given in Appendix E.

[2] Chert, or chert forming material, i. e., opal or chalcedony, or other reactive material, i.e., rhyolite, obsidian, andesite etc.

for decrease in the silica-producing reaction as the available alkalies are more rapidly depleted by absorption and liberation of silica over the greater and greater surface area exposed to attack."

The total percent expansions of the bars (11 months) and their pessimum proportions are given in Table 6 (page 42). Graphs showing percent expansion at 2, 6, and 11 months versus concentration of chert are presented in Figure 18.

Explanation of Mortar-bar Expansion Graphs, and Conditions of Storage

In the mortar-bar expansion graphs percent expansion is plotted against percent chert. Each number along the horizontal axis (5, 10, 20, etc.) represents a mortar-bar with that concentration of chert. (Actually two bars since duplicate bars were fabricated.) Every month the percent expansion of each mortar-bar is plotted on the appropriate vertical line representing the concentration of chert in that mortar-bar, and the points are connected by a line numbered for that month[1]. The dashed line represents a duplicate set of mortar-bars which were stored in a different container. In three cases (Samples 57, 44, and 45) the dashed line is notably lower than the corresponding solid line for the later months. The discrepancy is attributed to operational problems in maintaining the same degree of moisture in both mortar-bar containers. The container with the duplicate bars was observed at times to be deficient in moisture relative to the other container. Since it is known that abundant moisture is necessary for maximum expansion, it is assumed that the lower expansion of some of the duplicate bars (dashed line) is due to lack of adequate moisture.

Results

As can be seen from Figure 18, all of the cherts with the exception of No. 45 have exceeded .1% expansion within 12 months, the presently accepted ASTM limit separating deleteriously expansive from non-deleteriously expansive materials.

Four of the five deleteriously expansive cherts exceed .1% expansion at concentrations other than the pessimum proportion. This information is tabulated below:

Chert Sample	Range over .1% expansion (% chert)
57	20 - 75%
44	10 - 75%
57-B	5 - 50%
73	10 - 75%
55	50% Pessimum Prop only
45	Not over

[1] Only the 2, 6, and 11 months measurements are shown in Fig. 18 for purposes of clarity.

MORTAR BAR EXPANSION GRAPHS
PERCENT EXPANSION VS. PERCENT CHERT
ELEVEN MONTHS

——————— SET OF MORTAR BARS STORED IN (A) CONTAINER

– – – – – DUPLICATE SET OF MORTAR BARS STORED IN (B) CONTAINER

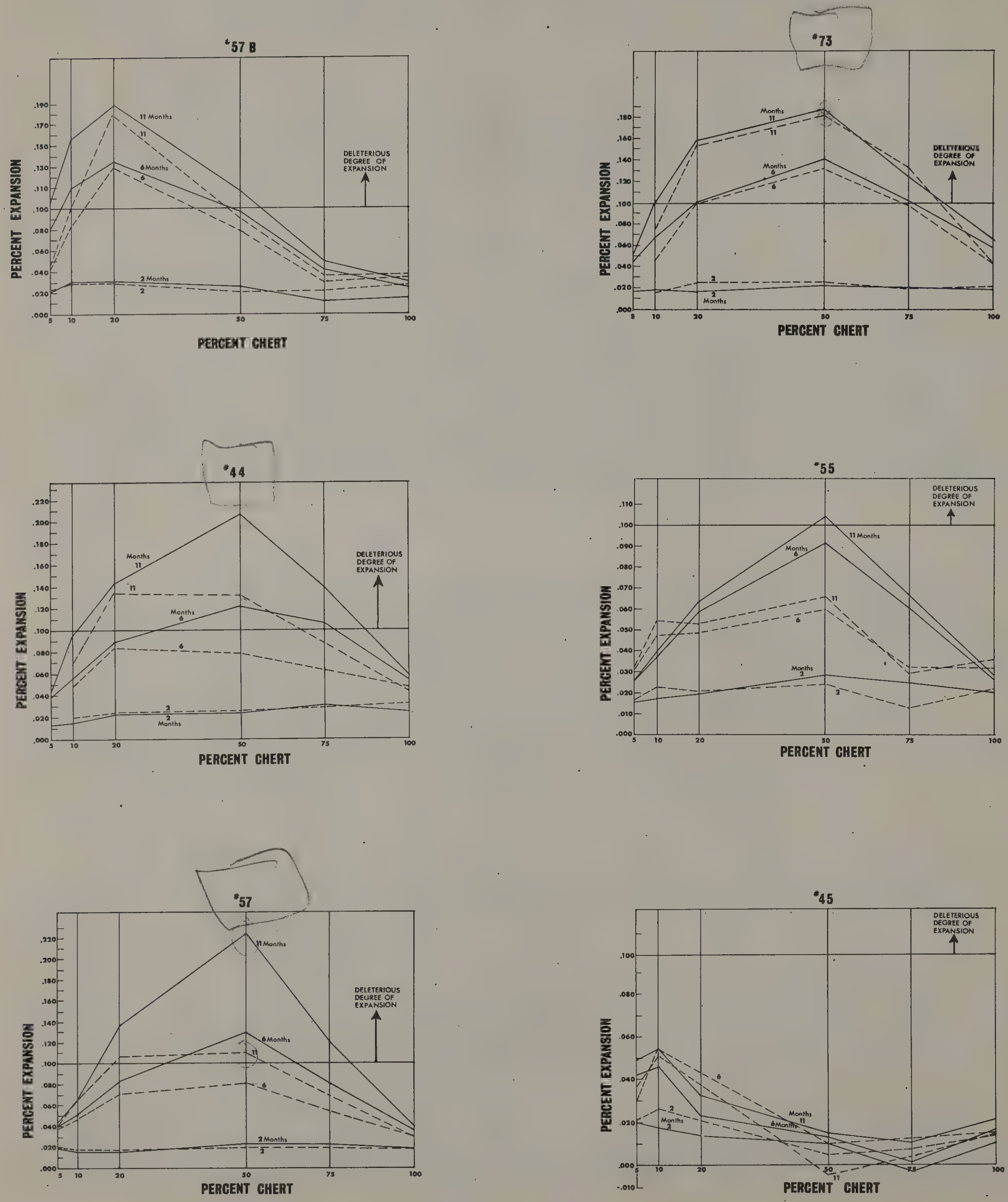


FIG. 18. MORTAR-BAR EXPANSION GRAPHS.

Examination of Mortar-Bars

An examination of the mortar-bars was made at the time of the ten-months measurement for percent expansion and at 11 months just prior to their being broken for preparation of thin sections.[1]

Systematic examination of the six bars in each of the six test sample groups has permitted the following observations:

(1) No severe cracks or pop-outs were observed on any of the bars, but microscopic examination of the thin-sections of the bars revealed fractures which transect chert particles and extend out into the cement paste, commonly fracturing other adjacent particles. Note: The numerous black spots which appear in the photographs of the mortar-bars are cavities or pits in the surface which result normally during the fabrication of the bars. They are not "pop-outs," nor do they reflect the influence of any abnormal process. Many of them have, however, as noted below, served as avenues of exit for substances produced by a reaction in the interior of the bars.

(2) All bars to some extent, but particularly the pessimum and adjacent bars, displayed features of the following description:

> (a) A white or gray, scaly, hardened, frequently translucent, efflorescence within and surrounding voids, pits, or irregular cavities in the mortar-bars. Larger areas of this substance are shiny, and may show a network of fine cracks or crazing. Close-up photographs of these features are shown in Figures 25-28.
>
> (b) A watery fluid on the outside of the bars in the vicinity of material described in (a) above and associated with long white stains running the length of the bars. These are well displayed in Figures 19 and 20.

(3) In a roughly quantitative manner the maximum development of features (a) and (b) above can be correlated with the mortar-bars showing the maximum expansion.

In the photographs (Figures 19-24), the six bars in each sample group are laid out according to increasing percentage of chert. It can be seen that in all cases the bar containing the pessimum proportion and the bars containing percentages of chert closest to it display maximum development of the surface features. In all cases the bars containing percentages of chert farthest away from the pessimum proportion show the least development of these features.

1

Complete discussion of the thin sections is not included in the present paper because the preparation of the thin-sections, which took about 3 months, had to await the completion of the mortar-bar test. When the thin-sections were returned, many parts of the report were nearing completion and it was judged that detailed examination of the thin-sections would slow up the remaining work. Results of the thin-section examination will be included in the final report.

Four samples have a pessimum proportion of 50%. Figures 19, 20, 22, 23. For these samples the bars containing 5% and 100% chert show little if any desiccated-gel surface features, but the pessimum bar (50%) and the percentages near to it (20, 75, and sometimes 10%) show surface features of the type described in (2) a) and b) above.

Also noteworthy is the observation that if the six sample groups are compared with each other, it is evident that the most expansive sample (#57) (as a group of six bars) shows the greatest amount of surface features and similarly the least expansive group shows the least surface features. There is a gradation between the two extremes. Information for this comparison is tabulated below:

Sample Number	Total Expansion pessimum bar %	Figure Number
57	.225	19
44	.215	20
57-B	.200	21
73	.190	22
55	.105	23
45	.055	24

Figures 25-28 show surface features of the desiccated gel in greater detail. The area of each large scale photograph is indicated by a black circle on the photographs of the mortar-bars. The photographs illustrate the powdery, caked, and glazed appearance of the desiccated alkali-silicate gels. Certain ones (Figure 26) demonstrate that the substances have been extruded from the small holes in the surface of the mortar-bars.

Figure 27, is a comparison of the surfaces of two mortar-bars from the same sample group. Figure 27a showing well developed gel features and Figure 27b showing an essentially unaffected surface. Bar #28 (Fig. 19) was the most expansive of all 36 bars with a total expansion of .225%. Bar #30, containing 100% of the same chert as Bar #28 expanded only .045%, or about 20% of the expansion of #28. Comparison of the two mortar-bars illustrates that the extent of development of surface features is proportional to the expansion of the bar.

Considering its appearance and its association with the most expansive mortar-bars, there is little doubt that this material which has been described as desiccated-gel surface features is the product of a reaction between the cement and the aggregate. McConnell et al (15) in describing the appearances of "gels" produced by cement-aggregate reaction made the following applicable observations:

(1) The products of cement-aggregate reaction appear as exudations on external surfaces. They may be watery, viscous, or hard and brittle--all in close association.

(2) They may be colorless and transparent or white and porcelaneous. Both types frequently occur in the same deposit.

(3) Where moisture is available from external sources, the gels become dilute and watery in consistency.

(4) Where exposed to the atmosphere, the gels are rapidly desiccated and sometimes carbonated, becoming white and hard.

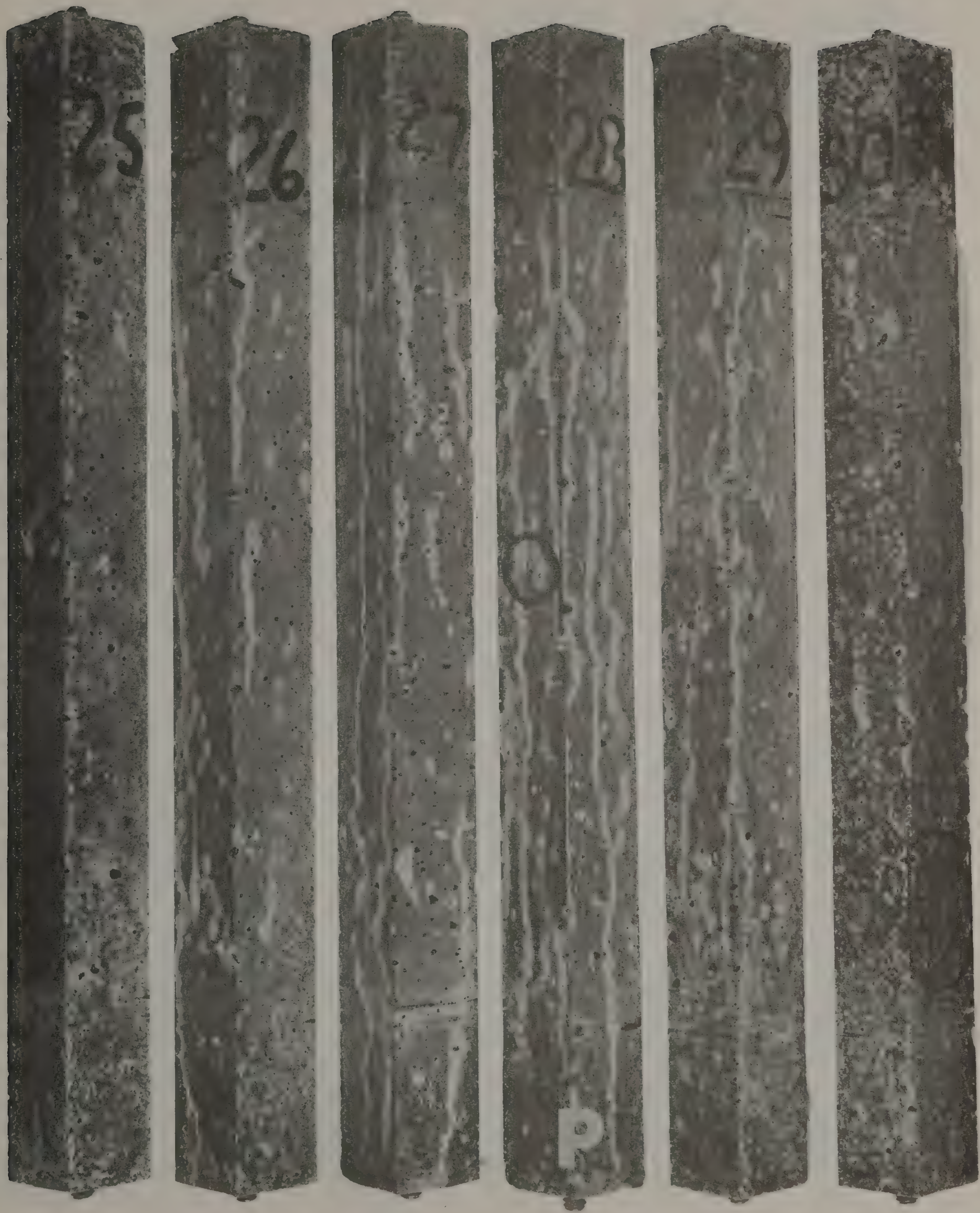
The conditions noted in (3) and (4), availability of moisture and atmospheric exposure, both obtain in the laboratory during the "life cycle" of the mortar-bars.

Explanation of Figures 19 - 24

The figures are arranged in order of decreasing total expansion from left to right. Thus Figure 19, sample #57 contains the bar with the highest total expansion, and Figure 24, sample #45 contains the bar with the lowest total expansion. This arrangement facilitates the comparison referred to on page 54, paragraph 1.

The pessimum bar (bar containing the proportion of chert which gave the highest total expansion) in each group is indicated by the letter P at the bottom of the bar. The percent chert in each bar is also indicated at the bottom of the photograph.

Areas enclosed by black lines were photographed at higher magnification and may be seen in Figures 25 through 28.



5 10 20 50 75 100

Percent Chert

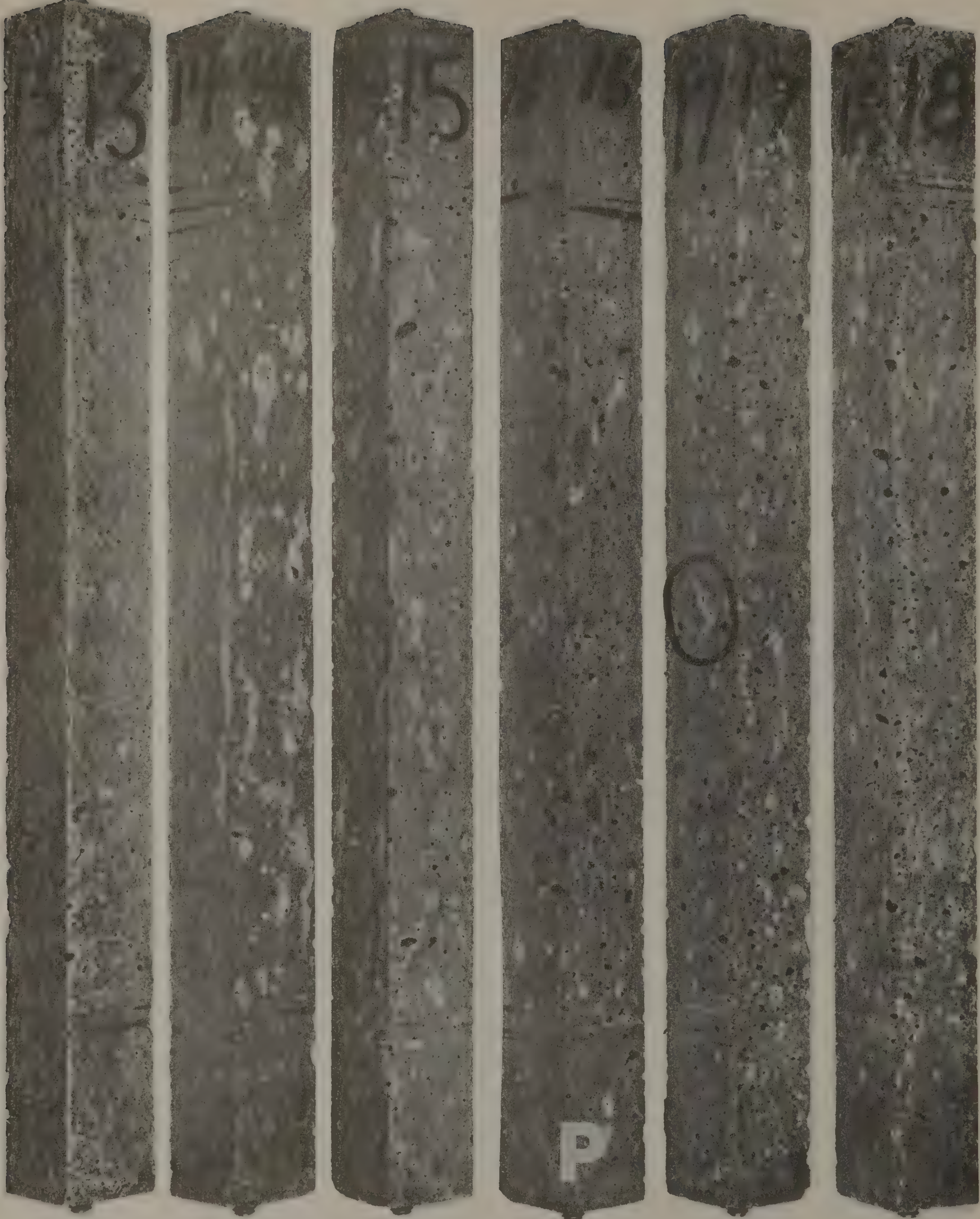
FIG. 19. PHOTOGRAPH OF SIX MORTAR-BARS MADE WITH SAMPLE 57.

FIG. 20. PHOTOGRAPH OF SIX MORTAR-BARS MADE WITH SAMPLE 44.

5 10 20 50 75 100

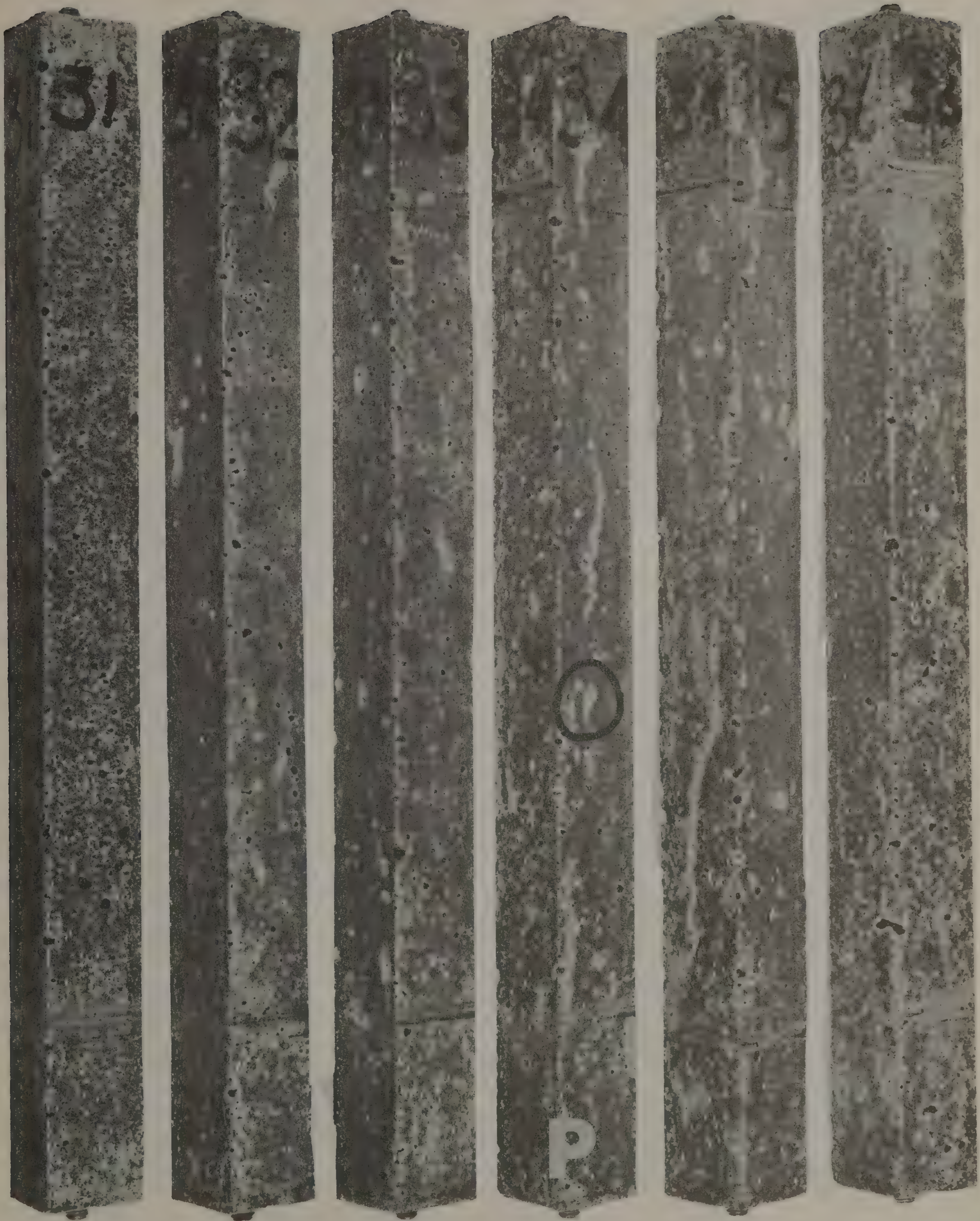
Percent Chert

FIG. 21. PHOTOGRAPH OF SIX MORTAR-BARS MADE WITH SAMPLE 57-B.



5 10 20 50 75 100

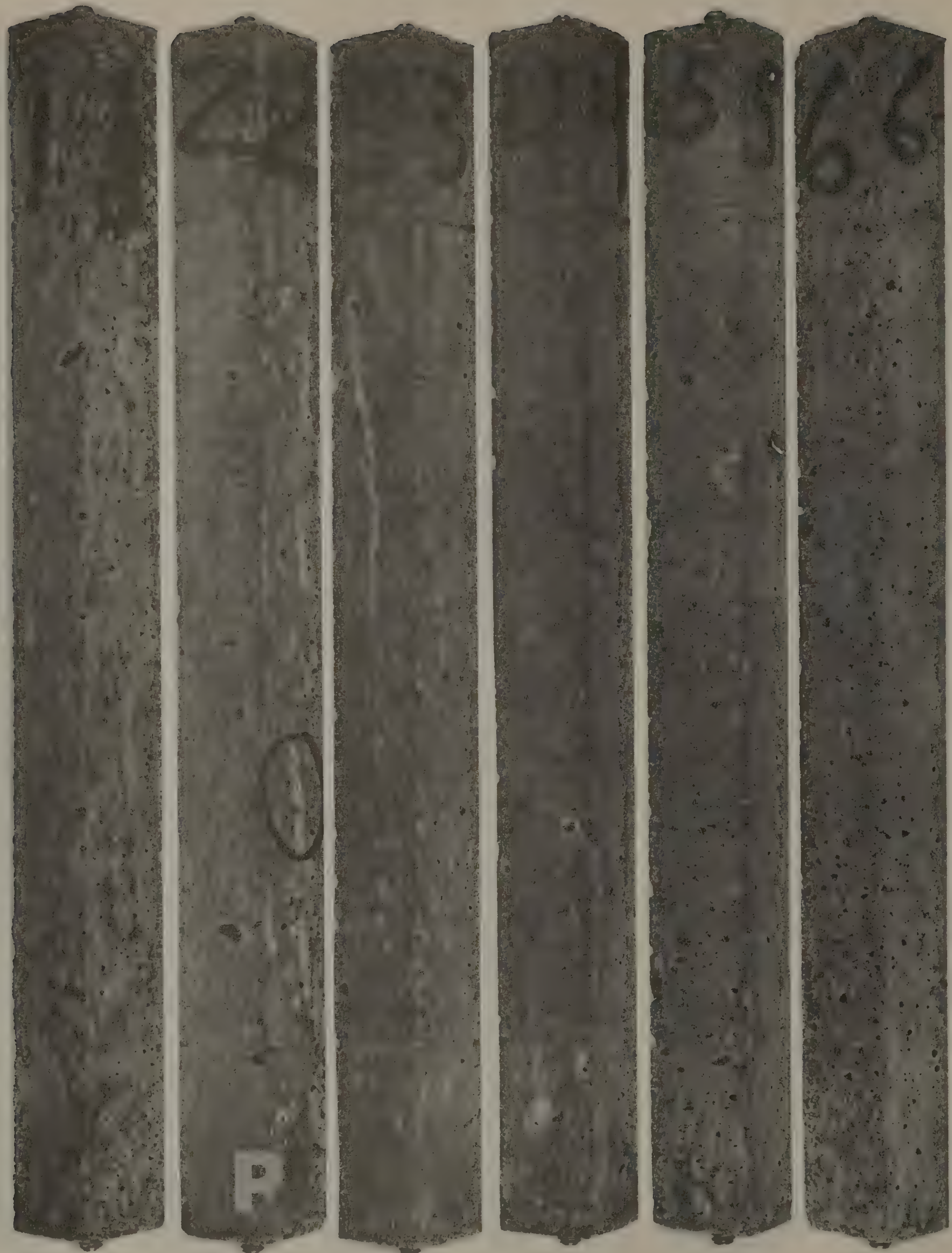
FIG. 22. PHOTOGRAPH OF SIX MORTAR-BARS MADE WITH SAMPLE 73.



5 10 20 50 75 100

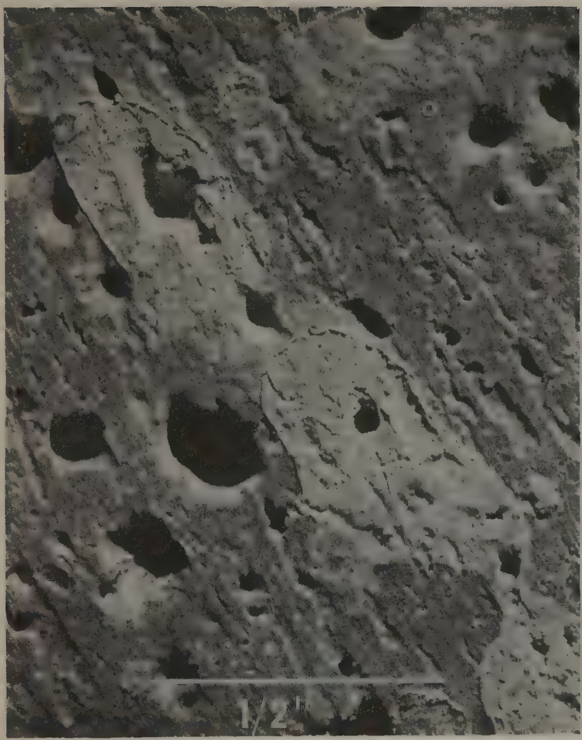
Percent Chert

FIG. 23. PHOTOGRAPH OF SIX MORTAR-BARS MADE WITH SAMPLE 55.



5 10 20 50 75 100

FIG. 24. PHOTOGRAPH OF SIX MORTAR-BARS MADE WITH SAMPLE 45.



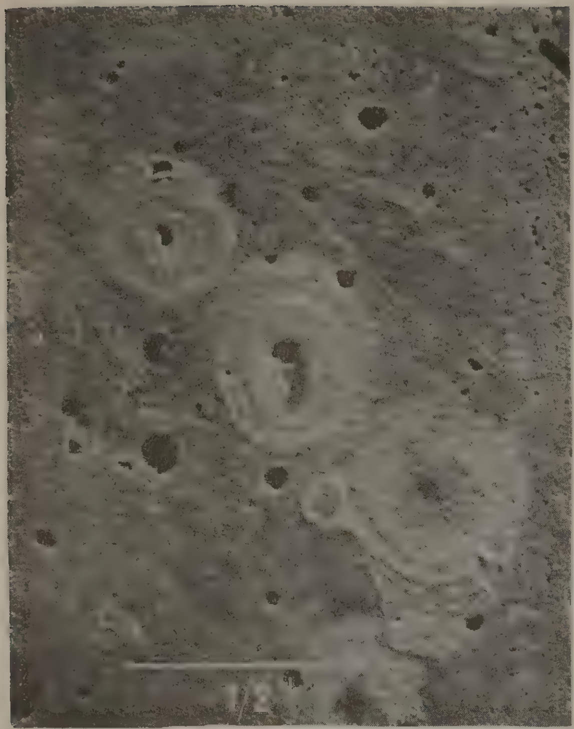
a. (left) Chert sample #45, Fig. 24, bar 2.

Typical view of an area of linear-shaped desiccated gel features. The linear shape is produced by the dripping of material down the sides of the bar while still in a liquid (or semi-liquid) condition. The dripping patterns run back over themselves because the bars are reversed end over end each month.

b. (right) Chert sample #57-B, Fig. 21, bar 7.

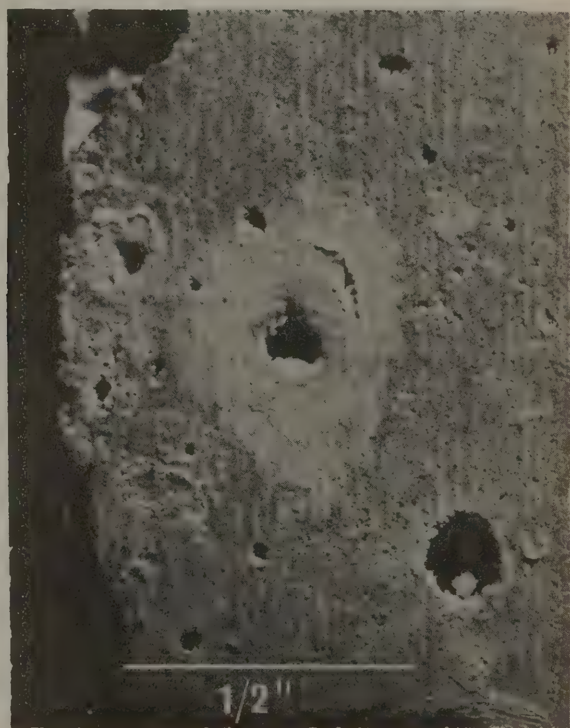
Desiccated caked gel features. Note glazed appearance and network of fine cracks (crazing).

FIG. 25. DETAIL OF GEL FEATURES ON MORTAR-BARS 2 AND 7.



a. (left) Chert sample #73, Fig. 22, bar 17.

Desiccated, glazed and cracked gel surrounding small holes from which it has extruded.



b. (right) Chert sample #44, Fig. 20, bar 22.

Small round gel feature, edge of bar in photo. This area is not outlined on bar 22 because it occurs on the underside of the mortar-bar.

FIG. 26. DETAIL OF GEL FEATURES ON MORTAR-BARS 17 AND 22.

a. (left) Chert sample #57, Fig. 19, bar 28.

Glazed, cracked, desiccated gel surrounding void from which it was extruded.

b. (right) Chert sample #57, Fig. 19, bar 30.

Close-up of relatively unaffected surface on bar containing 100% chert.

FIG. 27. DETAIL OF GEL FEATURES ON MORTAR-BARS 28 AND 30.

Chert sample #55, Fig. 23, bar 34.

Desiccated gel feature.

FIG. 28. DETAIL OF GEL FEATURES ON MORTAR-BAR 34.

DISCUSSION OF RESULTS

Relation Between Mortar-bar and Quick Chemical Test Results

As stated before, the five cherts which were excessively expansive (greater than 0.1%) in the mortar-bar test were also indicated to be deleterious in the quick chemical test. However, the sixth chert, sample #45 did not exceed 0.1% expansion even though the results of the quick chemical test indicated that it was deleteriously reactive.

Number 45, a "white" nodular chert with many fossil fragments and very dull, earthy luster, is characterized by the highest water absorption and lowest bulk and apparent specific gravities of any of the cherts tested.

Sample No.	Apparent s.g.	Bulk s.g. (dry basis)	% absorption
45	2.57	2.34	3.89
44	2.59	same	none
57	2.60	same	none
73	2.61	same	none
55	2.62	same	none
57-B	2.64	2.58	.85

With the exception of lower percentages of calcite and dolomite there is no evidence to indicate that the constituents in #45 are radically different than those found in the other cherts. The high absorption and low apparent and bulk specific gravities may then be taken as an indication of a relatively greater porosity than that found in the other cherts.

It has been noted by others (17, p. 212) (3, p.4) that a high absorptive capacity, resulting from high porosity and permeability of the aggregate, may accomodate some expansion by providing room for secondary reaction products, and thus act to reduce the pressure exerted against the enclosing cement paste. This explanation would account for the lower percent expansion of sample #45.

There is no readily apparent systematic relationship between position on the quick-chemical test plot and relative magnitude of expansion in the mortar-bar test. In Figure 29 the six cherts tested by the mortar-bar method are plotted separately with numbers indicating their relative total expansions.

A fairly good direct relationship exists between total expansion and magnitude of the ratio S_c/R_c. The data is shown in Figure 30a. Note that #45 does not conform well to the other data points. As explained previously it has certain physical properties which can prevent it from reflecting the expansion which would be expected from a consideration of its chemical character alone.

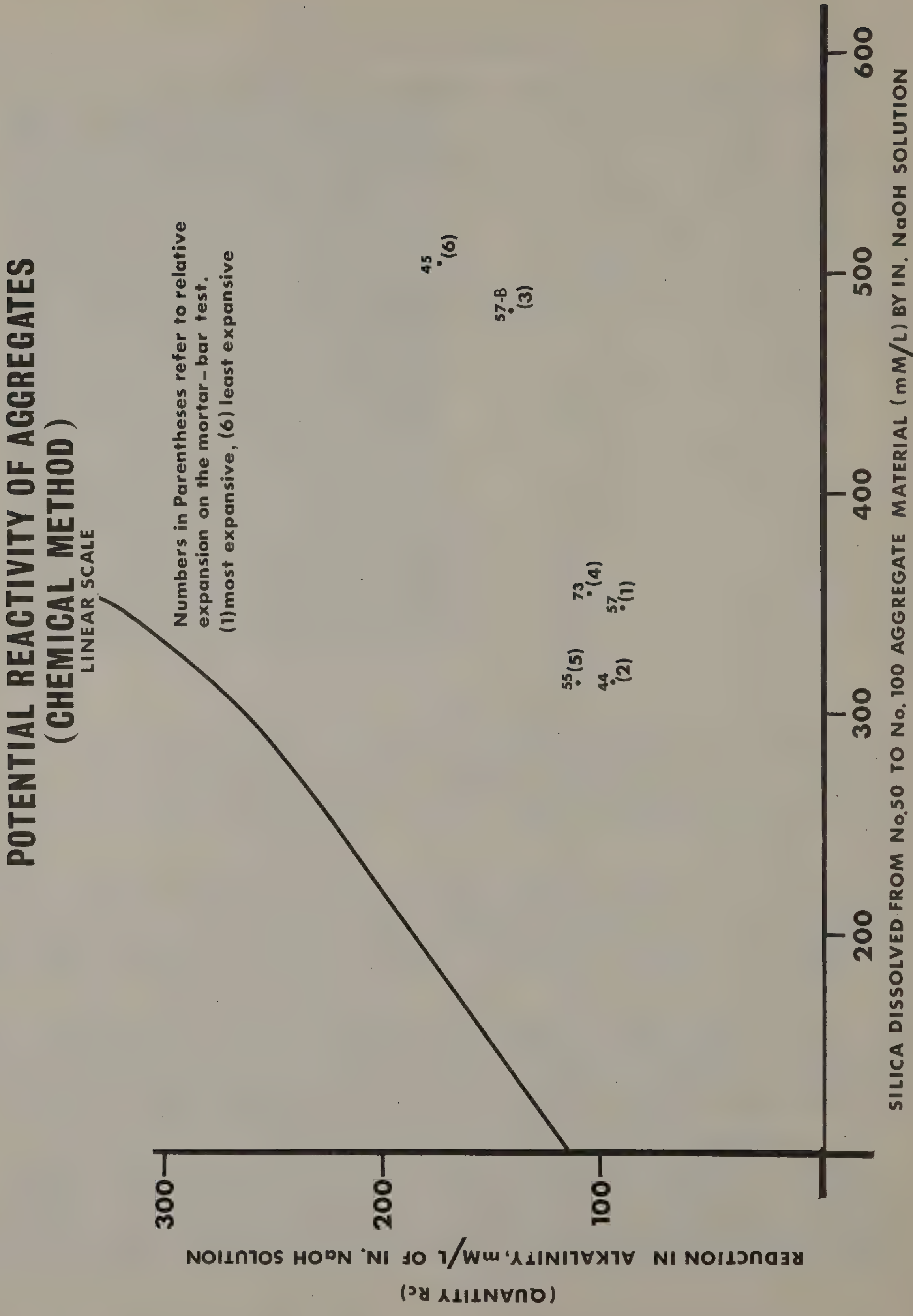


FIG. 29. RELATION BETWEEN RELATIVE MORTAR-BAR EXPANSION AND POSITION ON THE QUICK CHEMICAL TEST PLOT.

The relationship shown in Figure 30a is an "ideal" correlation between quick-chemical and mortar-bar results, i.e. reactive materials are characterized by an S_c/R_c greater than 1. All other things being equal, the greater the magnitude of the ratio S_c/R_c, the greater should be the expansion.

Relation Between Alkali in Chert and Alkali Reactivity

All of the cherts contain small amounts of the alkalies Na_2O and K_2O. Concievably alkalies occurring in certain minerals within some aggregates may contribute to the total alkalies available for reaction. A mechanism by which this may take place has been postulated by Halstead and Chaiken (10):

> "The alkali hydroxides may also be derived from alkali-containing zeolitic minerals if these are present in the aggregate as a result of a reaction in which the lime from the cement displaces the alkali from the zeolites. In most cases, however, the alkalies are derived from the cement."

The zeolites are a family of hydrous silicates which may contain sodium, potassium, and calcium in their structure. They are secondary minerals which are found most characteristically in cavities and veins in basic igneous rocks (5). It is unlikely that the Onondaga cherts contain any zeolitic minerals.

The alkalies in the Onondaga cherts are probably in clay minerals or detrital silicates. Since detrital quartz grains were observed in cherts and the associated limestone, a small amount of detrital feldspar such as albite (which contains sodium) might also be present. The potassium is probably in a clay or micaceous mineral such as illite or sericite.

Because of the stability of these minerals, probably little if any of their alkalies are available for augmenting the alkalinity of the environment. However, an analysis of the data cannot rigorously exclude the possibility that if another variable is operating, the alkalies in the cherts may have contributed to the total expansion. Thus, in the mortar-bar tests those cherts with high alkalies (73, 57, 44) had high expansions, but 57-B, which is low in alkalies, also had a comparably high expansion.

A long range effect, such as the regeneration of alkaline solutions in "old" concrete utilizing some alkalies contributed by the aggregate, is a possibility which should receive consideration, but will not be discussed here.

Relation between Petrography of Chert and Results of the Quick Chemical and Mortar-Bar Tests

The range of expansion between the four cherts (57, 44, 57-B and 73) with the highest total mortar-bar expansions was slight (see Table 6) and the differences are not regarded as significant enough to correlate systematically with petrographic features. If they are regarded as a group, as petrographic and chemical evidence indicates they might be, then there are significant differences between them and #55, the chert with the second lowest percent expansion.

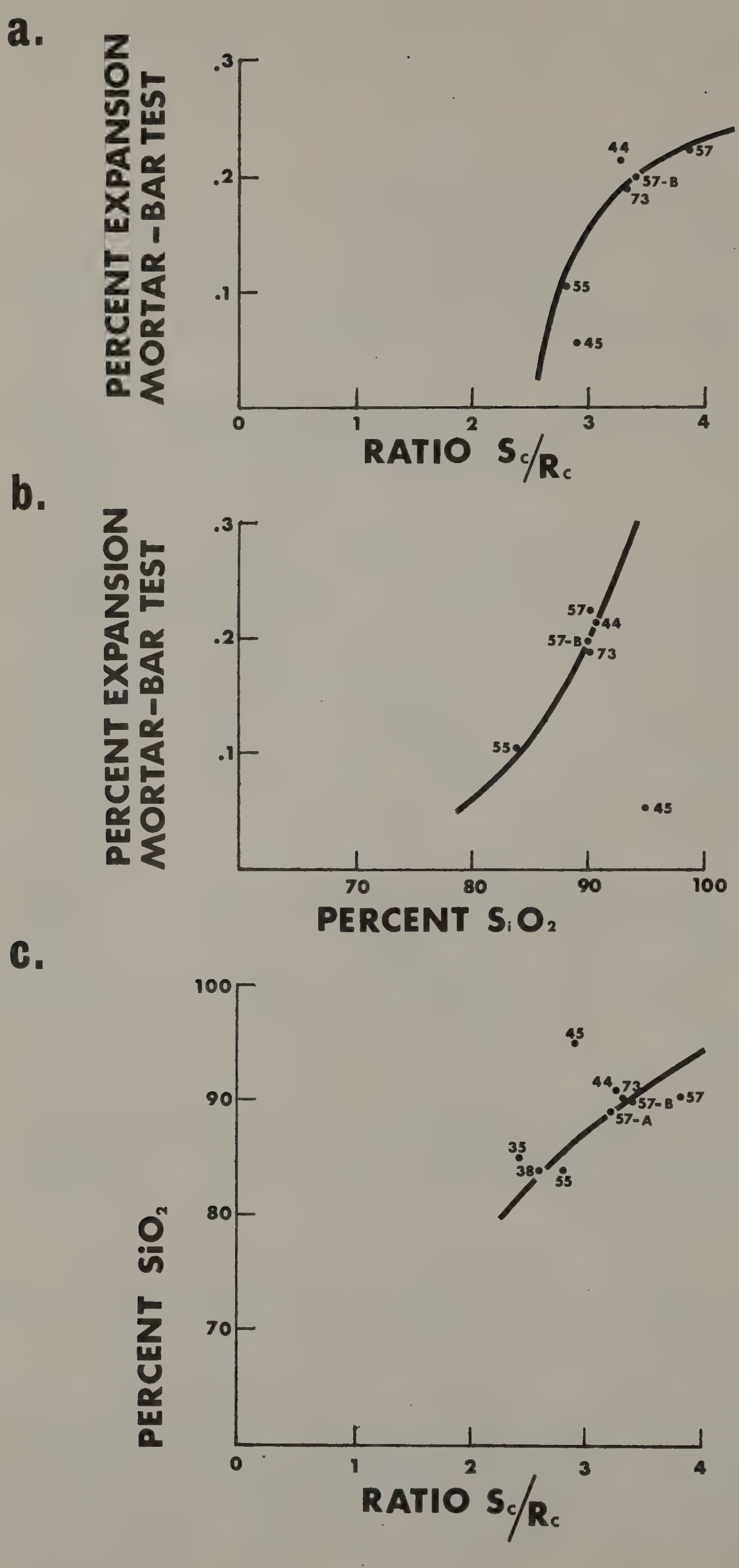


FIG. 30. RELATION BETWEEN: MORTAR-BAR EXPANSION VS. S_C/R_C, MORTAR-BAR EXPANSION VS. % SILICA, % SILICA VS. S_C/R_C.

Chert #45, the chert with the lowest mortar-bar expansion is a special case and will be discussed at the end of this section.

Cherts number 57, 44, 57-B, and 73 are characterized by areas of variable texture. The main groundmass grades into coarser or finer regions of microcrystalline quartz which are fairly clear in plane light and bright in x-nicols. Within the groundmass are areas of chalcedony, cryptocrystalline quartz, and megaquartz which usually replace or are contiguous to fossils. Dolomite crystals are evenly distributed, but if there is any calcite or remnant limestone, it tends to be in patches.

The principal differences between #55 and the four most expansive cherts are: (1) The more even texture and slightly coarser grain size of #55. (2) The higher percentage and more even distribution of remnant carbonate material in #55, - the groundmass is dusty in plane light and murky in x-nicols. (3) The fossils in #55, are largely replaced by microcrystalline quartz rather than by chalcedony, cryptocrystalline quartz and/or pseudoquartzite as is the case in the other cherts. There is some cryptocrystalline quartz (which may or not be related to fossils) but little chalcedony.

There is a better relationship between the results of the quick chemical test and the petrography of the cherts (which is discussed below) than there is between the mortar-bar results and petrography. This is due to the fact that there are more points on the quick chemical test plot and a greater spread of values between them. Each point on the quick chemical test plot is represented by one or more thin-sections which have been examined in detail. Detailed descriptions for the six most important samples, those subjected to both quick chemical and mortar-bar tests, are presented in APPENDIX A.

With reference to Fig. 15 (page 44): The results of the quick chemical test when plotted on a log scale are limited in their usefulness for research purposes. The points are cluttered and the spread of values is not evident enough.

Plotting on a linear scale, see Figure 31, is more useful for correlating quick chemical test results with other data since the true range of values is accurately represented. Also continuous variation between end-member types[1], which is so important in geological considerations, may be more easily observed.

A qualitative characterization of the microscopic appearance of the two "end-member" types of less expansive and more expansive cherts, whose characteristics have been cataloged by observation of trends and gradations between the chert samples, is given below. It is illustrated diagramatically in Figure 31.

In Figure 31 note that the distribution of points suggests that there is a more or less continuous range of values across the field from cherts that may be loosely described as potentially less deleterious or expansive (Region I on Figure 31) to those loosely described as potentially more deleterious or

[1] An end member is: One of two or more distinctive forms (or things), characterized by a maximum value of some property or properties, between which more or less gradual and continuous variation occurs. - Adapted from (8)

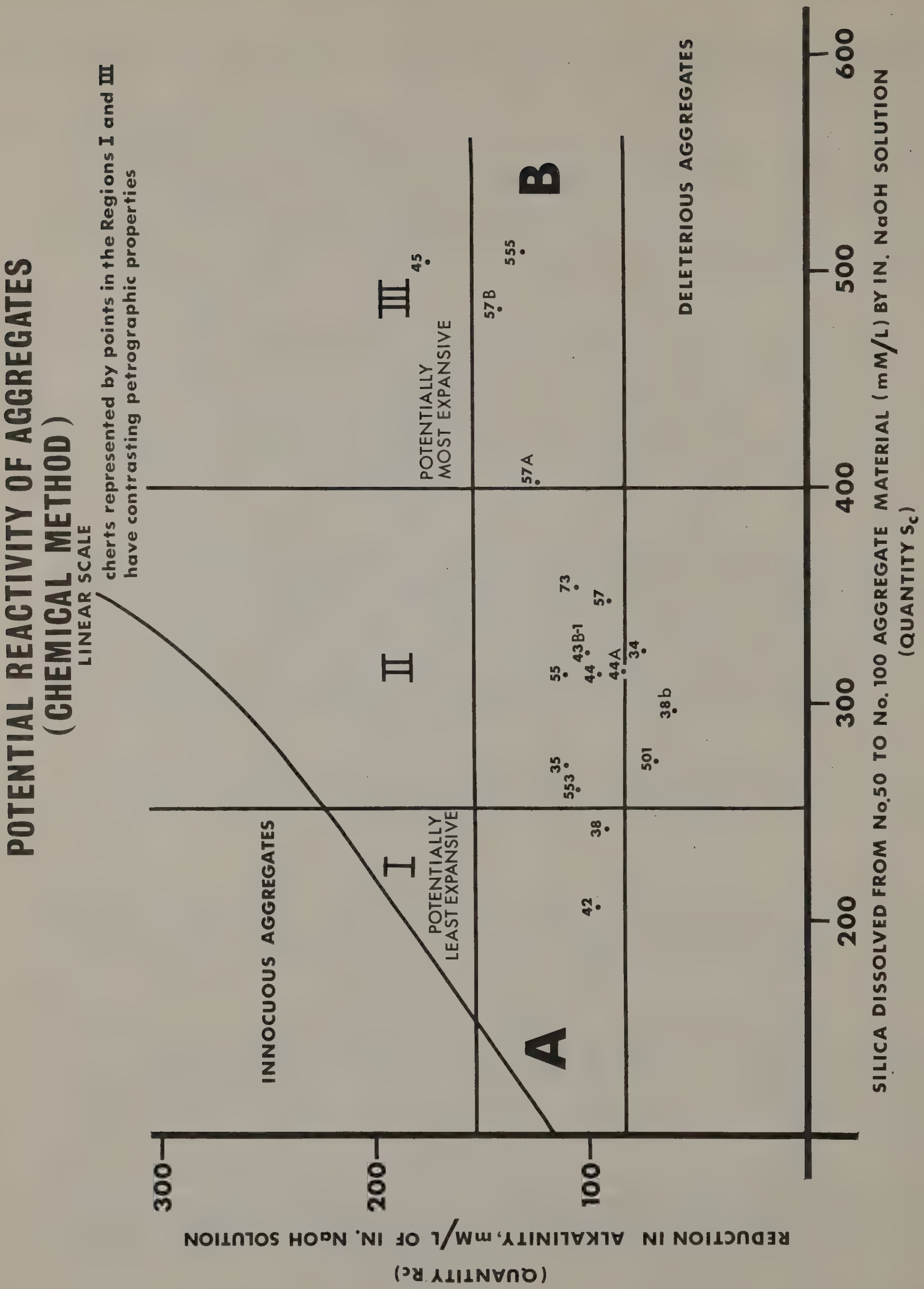


FIG. 31. RELATION BETWEEN REACTIVITY OF CHERT AND PETROGRAPHY.

expansive (Region III on Figure 31). The two extremes in the areas of #42 and #45, are characterized by contrasting petrographies. The contrasting characteristics overlap in the central portion (Region II, Figure 31). Most of the samples fall into this region.

Less Deleterious Chert Regions I to II	More Deleterious Chert Regions II to III
1) High percentage of carbonate in x-nicols (excluding dolomite)	1) Low percentage of carbonate in x-nicols (excluding dolomite)
a) generally murky or darker in x-nicols; poor contrast between light and dark areas in microcrystalline quartz	a) brighter in x-nicols, good contrast between "grains" of microcrystalline quartz.
b) dusty or clouded in plane light	b) clear, uniformly colored in plane light
c) change of relief when rotated in plane light	c) little or no change of relief when rotated in plane light
d) high percentage of remnant limestone which tends to be uniformly distributed	d) if above average percentages of carbonate are present, it tends to be localized in carbonate rich areas
2) Homogeneous appearance, groundmass composed largely of uniformly sized microcrystalline quartz	2) Variable in texture and grain size; composed of microcrystalline quartz, both fine and coarse grained, with subordinate areas of cryptocrystalline quartz. The variations in texture are apparently related to amount, type, and distribution of fossils.
3) Little or no chalcedony, isotropic silica, or pseudoquartzite	3) Likely to have areas of chalcedony, and some isotropic silica and pseudoquartzite.
4) Few areas in which index of refraction of groundmass can definitely be stated to be lower than balsam.	4) May have localized areas of "colloform" structure with index of refraction lower than balsam.

The correlation between petrography and the results of the quick chemical and mortar-bar tests agrees with the relationship discussed earlier--that percent expansion appears to be proportional to the magnitude of the ratio S_c/R_c. Thus, on Figure 31 note that between the letters "A" and "B" in the region bounded by parallel horizontal lines the ratio S_c/R_c increases from left to right. That is, along a single horizontal line R_c remains the same while S_c increases. In this case the ratio <u>generally</u> increases since the vertical distance (R_c from about 80 to about 160) is less than the horizontal distance (S_c from about 200 to about 500).

It can be seen that as cherts possessing petrographic properties characterized by Region I, least deleterious, pass into Region II and grade into Region III, most deleterious, the S_c/R_c ratio generally increases. Samples 57-B (and 45) and 38 are nearly type examples for Regions III and I respectively, but no sample exemplifies perfectly all of the characteristics attributed to either end member.

Thus, I, II, III, and the region A-B illustrate the point that the petrographic character of the most expansive and least expansive cherts is different, and that the ratio S_c/R_c increases as the petrographic character changes from Region I to III.

The inverse relationship (presented in the section on chemical analyses) between SiO_2 and CaO (Figure 13) supports the observation, based on petrographic analysis, that the degree of deleterious character of the cherts is partially a function of (and proportional to) total silica content.

Correlations between petrographic analysis, chemical analysis, and quick-chemical and mortar-bar behavior suggest that the difference between more reactive and less reactive Onondaga cherts is related to two things:

(1) The total silica content of the chert

and

(2) The particular characteristics of that silica fraction, which in turn depend on the physical and chemical properties and relative proportions of the various chert forming minerals which compose it.

The general relationship to total silica content is shown by Figure 30b in which percent expansion is proportional to percent silica and, by Figure 31 where the potentially most expansive cherts (Region III) are the most siliceous, as determined by petrographic analysis.

The relationship of reactivity to the petrography of the silica (item (2) above) is implied by Figure 30, b. and c. in which it is seen that cherts with the same silica content have different percent expansions, and different S_c/R_c ratios respectively. This situation is believed to be caused by differences in petrographic character which are not pronounced within the mortar-bar tested group, but which can be inferred from the study of all the cherts as a group. For example, of two cherts with the same silica content, the one with more even-grained, microcrystalline quartz and evenly distributed carbonate, etc. (as described for Region I) would be expected to be less expansive than the other with variable grain size, areas of chalcedony, and localized rather than evenly distributed carbonate, etc. (as described for Region III).

The situation where the cherts have different silica contents and different textures is more difficult to analyze, for example, a chert with high silica content but "uniform" (Region I) texture versus a chert with low silica content but "non-uniform" (Region III) texture. High silica content would tend to make the first chert more expansive, but "uniform" texture would tend to make it less expansive. Likewise, low silica content would tend to make the second chert less expansive, but "non-uniform" texture would tend to make it more expansive.

At present it is not clear how to "weigh" silica content and petrography against each other with respect to their individual contributions to the deleterious character of a chert.

The chert with the lowest percent expansion, sample #45, is characterized by certain properties which cause it not to conform to the relationships which may be drawn from the other cherts and their properties. No. 45 has a low expansion. This, as explained previously, is due to its high porosity. No. 45 possesses other anomalous properties with respect to its total expansion, S_c/R_c ratio, petrographic character, and chemical analysis, which are as follows:

> The petrography and chemical character of #45 would indicate that it should be very expansive, if not the most expansive of the cherts tested. But disregarding the lack of expansion due to its porosity (inferred from its relatively high water absorption) and projecting its S_c/R_c ratio to the curve connecting the other points (% expansion vs. S_c/R_c, Fig. 30a) we see that at best #45 would give an expansion of about .13%, still next to the lowest. If the S_c/R_c ratio of #45 were low, it would help to resolve its anomalous relationship to the other samples.

An erroneously low value for S_c would lower the value of the fraction S_c/R_c. Ideally S_c should reflect all the silica liberated from the aggregate while it is undergoing the quick chemical test. But it is possible that for very reactive aggregates more silica can be dissolved from the aggregate than is accounted for by the silica in solution (quantity S_c). This silica in a gelatinous form is probably retained upon and within the particles of the aggregate material. It would be reasonable to assume that the demonstrated absorptive properties of #45 would only aid in the retention of this gelatinous material.

The foregoing reasoning to account for the anomalous position of #45 on the Percent Expansion vs. S_c/R_c plot (Fig. 30a) is suggested by statements by Mielenz (17, p. 204, 207) who observes that:

> "The accumulation of gelatinous silica upon the No. 50-100 fraction (the size range used for the quick chemical test- ed.) undoubtedly would become increasingly significant with increase in the amount of silica dissolved in the NaOH solution;..."

Thus, under certain conditions, the ratio S_c/R_c might be abnormally low for highly reactive materials.

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APPENDIX A

DESCRIPTIONS OF COLUMNS IN STRATIGRAPHIC CORRELATION CHART

Description Column I

Interval (Sample 55 T.B. from this interval)

I-1 Limestone: Medium gray, massively bedded, medium to coarse grained, straight, blocky fracture. Local zones of well developed stylolites. Bedding thicknesses 2-8'. Locally very rich in fossil fragments.

Chert: Persistent horizons of large, compound nodular cherts about 1-4' apart, nodules 4-9' thick, spacing 2-12". The length of the nodules is 4-14" but variable. Where nodules tend toward coalescence, the spacing decreases and the length increases to about 36". Cherts present are; "white," fossiliferous, dull luster, "#45"type, sharp contact with matrix, brownish patches on interior. Brown, calcareous chert persistently outcropping along horizon. Sharp contact with matrix. Some chert horizons are locally coalesced into seams with sharp upper and lower contacts.

I-2 (Sample zone #55)

Limestone: Medium dark gray, bedding thicknesses 2-4', homogeneous, even textured, fine grained crystalline. Blocky fracture with slightly fibrous fracture surface. Local strong development of stylolites. Occasional thin, wavy, shaly partings. Lower 6' essentially chert free.

Chert: Discontinuous horizons of rounded nodules irregular in position. Brownish gray with irregularly developed light brownish gray rim material. Nodules generally 2" thick (lower part contains horizons of thicker (8") and longer (16") nodules); spacing 1-2"; horizons of nodules 6" to 2' apart.

I-3 Limestone: Medium to dark gray, medium to fine grained. Generally rough fracture surface. Local zones of stylolites and accumulations of fossil fragments. Occasional shaly parting; 15" interval of thin-bedded limestone in middle of section.

Chert: Generally medium dark gray, brownish gray, and medium light gray with waxy or resinous luster. Peripheral zones if present are yellowish gray, light gray, tan, or white. The varieties of chert occur as (1) scattered nodules, (2) swarms of nodules, sometimes coalescing into long stringers, and (3) large compound nodules. Cherts are 1-5" thick and have sharp contact with matrix.

I-4 (Sample zone 555 & 553)

Limestone: Massively bedded (2-8') with stylolites. Local areas of very coarse grain caused by accumulation of fossils and fossil fragments. Medium light gray to light brownish gray.

Chert: #555, Very light gray to yellowish gray with brownish interior, very fossiliferous. Occurs in upper half of interval in two horizons of nodules approximately 1' apart. Upper horizon 1-1/2" thick, 2-1/2-5" long, spacing about 3", not too persistent. Lower horizon-persistent nodules 2-4" thick, some coalesced into stringers 53-54" long; spacing about 1-3".

#553. Occurring in lower half of interval. Brownish gray, nodular cherts with poorly developed peripheral zone, some fossil specs. Nodules 2-4" thick, 1/2 to 1-1/2" apart, spacing 4-10".

I-5 Massive limestone: Medium gray-medium dark gray, variable grain size (fine to coarse), 1-2' bedding thickness, blocky fracture with irregular fracture surface. Cherts similar to 44A, 44, 43B-1.

Cherts of Massive ls: Brown, simple and compound nodules, with indistinct, thin peripheral zone. 2-3" thick, 4" long, spacing 1-3". Elongated stringers occur 2-5" thick, 14-15" long, 3-4" spacing.

Interbedded limestone: Dark gray, irregular, lensy, interbedded structure; fine grained, smooth curved fracture surface. Some intervals argillaceous with subordinate bedding planes.

Chert of interbedded limestone: Light brownish gray to medium light gray, waxy luster. Occurs in bands of irregular shape which migrate vertically. Interspersed small rounded nodules occur between bands. Bands are 1' long, 2-4" thick.

I-6 (Sample zone 57-A)

Limestone: Medium dark gray, fine-grained, subordinate bedding planes 6-12" apart; smooth slightly curved fracture surface. Irregular bedding due to interspersed argillaceous zones about 1/4" thick.

Chert: Medium dark gray to dark bluish gray, resinous luster; sharp subconchoidal fracture; occasional milky white veins of chalcedony. Occurs in elongated stringers with protuberances. Interspersed smaller nodules occur between stringers. 1-2" thick, 15" long, spacing 1-4", stringers 3-6" apart. Sharp contact with matrix; little zone material.

I-7 (Sample zone 57-B)

Limestone: Medium to light gray, massively bedded, medium to coarse grained. There are local areas of very coarse grain (2-4 mm) and rough fracture and local areas of fine grain and smooth fracture.

Chert: Mottled white, gray, to light brownish gray, blocky irregular fracture; dull luster; calcareous patches, and vugs filled with drusy and crystalline quartz. The chert occurs in broad bands (3-12" thick) which anastomose vertically and enclose "islands" of limestone, but which also display a fairly strong alignment parallel to the bedding. The broad bands of chert generally have a sharp contact with the limestone, but within the areas of chert there are patches of limestone (usually partially silicified) having a diffuse gradational contact with the chert.

I-8 (Sample zone 57)

The dark limestone and chert component is sample #57.

Limestone: Medium dark gray to dark brownish gray; massively bedded, but with subordinate breaks because of stylolites, shale and interbedded chert. Medium to fine grained; fracture varies from rough straight to smooth curved.

Chert: Mottled light and light bluish gray to medium dark gray and dark bluish gray. Dull resinous luster, subconchoidal fracture. Occurs in elongated seams or stringers with irregular top and bottom; interbedded with limestone, shaly material, and stylolites.

Edgecliff beds. Ls: Brownish gray to light brownish gray, massive (1-4' beds), coarse grained (1/2-2mm), stylolitic; may be chert free. Chert: Mottled and clear bluish gray, thickness 1-4", spacing about 6", length 7-15"; sharp contact with matrix. Stylolites may form boundary of nodules.

I-9 Limestone: Occurs as (1) thin beds between thick intervals of chert, and (2) stringers, blebs or laminations within the chert. Chert: slightly mottled, medium gray to light gray, dull luster, smooth fracture, stylolitic. Contains calcareous patches and remnants of fossils.

1-10 Limestone: Brownish gray, fine-grained, dense, fossiliferous, smooth fracture, wavy shaly laminations. Occurs in (1) beds (3-6" thick) between thicker chert rich intervals, and (2) stringers, blebs and laminations within chert.

Chert: Mottled dark gray to dark bluish gray, resinous luster, smooth conchoidal fracture. Stylolites and shaly partings are present.

I-11 Limestone: Light brownish gray, massive, medium to coarse grained (1-1.5mm) crystalline limestone. Rough fracture surface. Local very fossiliferous zones; some shaly partings.

Chert: Not abundant; occasional blebs of bluish gray chert. Darker patches in limestone may represent areas of incipient chert.

Description Column II

II-1 (Sample zone #45)

Limestone: Medium gray to light brownish gray, massive, medium to fine grained. Blocky fracture with very rough fracture surface; occasional thin, wavy, shaly laminations. Local zones of coarser grain caused by accumulation of small fossils and debris. Where weathered this forms a "pebbly" surface standing in relief.

Chert: White or light gray to brownish gray, nodular chert. Commonly with brownish interior. Poorly developed thin and discontinuous peripheral zone may be very light gray to yellowish gray. Sharp contact with matrix. Dull earthy luster, blocky fracture, fossiliferous. Occurs in rounded, simple, sometimes compound nodules, 1-4" thick. 2-10" long, in horizons or seams generally 3-24" apart. Spacing variable. Some horizons coalesced to form seams.

II-2 (Sample zone #44A)

Limestone: Medium gray to dark brownish gray, massive, medium to fine grained, smooth fracture surface.

Chert: Dark gray to bluish gray, dense, waxy luster, sharp fracture, no peripheral zone. Occurs in bands 2-3" thick (in upper half), 6" apart, and in dispersed round nodules in lower half. The bands may not be completely coalesced in which case the appearance is of nodules outcropping along horizons.

II-3 Limestone: Medium gray, massive, fine grained, smooth fracture. Chert: Brownish to bluish gray, resinous waxy luster. Peripheral zone absent, or thin and poorly developed. Bands 2-3" thick, 7-8" apart. Smaller round nodules dispersed between more prominent chert bands.

II-4 (Sample zone #44, 45C, 45R)

<u>Limestone</u>: Medium gray, massively bedded with subordinate breaks, fine grained. Dark fossil fragments and smooth, slightly curved fracture.

<u>Chert</u>: Brownish gray, waxy resinous luster, sharp fracture, occasional thin or poorly developed peripheral zone. Sharp contact with limestone matrix. Occurs in persistent bands 6-12" apart, 2-3" thick, which are elongated nodules. Smaller round nodules are dispersed between the more prominent chert bands. Samples No. 45C and 45R for rim-chert-limestone comparison analyses were taken from this interval at location No. 45, where the peripheral zones are more strongly developed than at location No. 44.

II-5 <u>Limestone</u>: Bluish gray, massive, essentially chert free, medium to coarse grained. Fibrous, elongate fracture with rough, fracture surface; fossiliferous.

II-6 (Sample zone 43B-I)

<u>Limestone</u>: Medium light gray to medium gray; irregularly bedded, fine grained, crystalline. Elongated, fibrous fracture, diffuse patches of zone material. Wavy, shaly partings are interbedded with limestone and chert.

<u>Chert</u>: Dark brownish gray to medium dark gray, resinous luster; hair-line cracks, smooth subconchoidal fracture. No regular peripheral zone, but zone material is irregularly interspersed with chert and limestone. Chert occurs as elongated knobby stringers.

II-7 <u>Limestone</u>: Dark gray, irregularly bedded, medium to fine grained, with shaly partings. <u>Chert</u>: is sparse, but occurs in small scattered nodules.

II-8 Edgecliff lithology, massive, chert free, crystalline limestone.

II-9 Lensy interbedded dark stringers of chert and dark gray limestone. <u>Chert</u>: 30%.

II-10 Edgecliff lithology: <u>Chert</u>: About 20%, white or light gray, resinous luster.

II-11 Lensy, interbedded dark chert and dark ls. <u>50-55% chert</u>. Locally may be very intergraded and coalesced. <u>Limestone</u>: smooth fine-grained. <u>Chert</u>: Mottled with little or no zone material.

II-12 Interbedded chert & limestone. Chert, 30%.

Limestone: Light gray, medium to fine grained.

Chert: Mottled light brownish gray, waxy resinous luster, sharp blocky fracture.

II-13 Edgecliff lithology with a few nodules of "#35" type chert.

II-14 Irregular interbedding of dark chert stringers and dark smooth fracturing limestone.

II-15 Limestone: Light to medium gray, medium grained, even textured, crystalline. Straight fracture with rough gritty surface. Local strong development of shaly laminations. The limestone is confined to irregular beds between and in chert.

Chert: Occurs in anastomosing network, migrating, irregular nodules, with no bedded character. Mottled in color, very light gray, light bluish gray, light gray, the colors intergrading with each other. Resinous luster, sharp, hackly fracture. Irregularly distributed zone material is yellowish gray.

II-16 Limestone: Light gray to brownish gray, massively bedded, medium to coarse grained (1-2mm), crystalline. Straight blocky fracture; may be very fossiliferous in lowest part.

Chert: Sparsely developed, mottled bluish gray, "35" type nodules 2-3" thick, fairly persistent.

Description Column III

III-1 Limestone: Massive, fine-grained, brownish gray; beds 1' to 4' thick; smooth, slightly curved fracture; occasional shaly zones and wavy shaly partings. There are evenly distributed small fossil fragments and some stylolites. The lowermost 5' (approximately) is a section of thick cherts in massive limestone.

Chert: Thick (6-8") layers with regular top and bottom (in lowermost section). Interspersed smaller nodules and lenses occur between the layers. Dark brown, with thick buff or tan peripheral zone; calcareous with blocky fracture.

III-2 (Includes sample zone #73)
Limestone: Fine-grained, dense, medium gray to brownish gray; smooth slightly curved fracture.

Chert: Irregular compound nodules, mottled in color; medium brownish gray to light gray with a light gray peripheral zone which may be poorly developed. Nodules are irregularly bedded with many coalescing horizontally and vertically to form an anastomosing network. Beds of chert are about 3-4" apart (1' in lower section). Nodules are 2 to 4" thick, 18-24" long.

III-3 Limestone: Fine grained, brownish gray, containing some stylolites and fossil fragments. Chert is sparse in upper part.

Chert: Brownish gray to light olive gray; smooth subconchoidal fracture; hairline cracks. Most nodules have well developed brown to light brown peripheral zones, or rims, approximately 1/8" thick.

III-4 Limestone: Essentially chert free, dark gray to medium dark gray, medium to fine grained, shaly and/or silty; rough fracture surface which may be fibrous or elongate. This lithology is generally equivalent to IV-2 and V-3d in the columns further east, but has more frequent "purer" intervals of lighter colored, homogeneous, crystalline limestone. Characteristic features of this lithology by which it is recognized here and in Columns IV, V, and VI, are: (1) Small (1 to 5mm long, and 1 to 2mm thick) tubular, oval shaped, or elongate light and/or dark colored areas in the limestone which are sub-parallel to the bedding. The color of the ovals usually contrasts with the background limestone, i.e. either light ovals in dark limestone, or dark ovals in lighter colored limestone. (2) Thin, small (.5 to 1mm.), curved, medium to light bluish gray, sharp pointed shells and shell fragments which are parallel to the bedding. (3) Intervals (approximately 3 to 6" thick) of very dark gray, almost black, argillaceous and silty limestone sometimes bearing small pyrite nodules. The limestone has fibrous elongate fracture but little shaly character such as thin-bedding or laminations.

Chert: Very sparsely developed, there are occasional hard, dark, siliceous "stains" or incompletely silicified zones of incipient chert in the limestone.

III-5 Limestone: Brownish gray, fine-grained, occasional stylolites.

Chert: Medium gray; sharp contact with limestone matrix; no peripheral zone type material.

III-6 Generally as III-4 above-chert free.

Limestone: (Upper 2') Well developed bands of dark, silty and argillaceous limestone, including small curved shells and light and dark elongate ovals. The lower 2 1/2' consists of mottled limestone with purer bands alternating with slightly silty and argillaceous bands.

III-7 Limestone: Light brownish gray; medium to fine-grained; wavy shaly laminations; many fossils and fossil fragments.

Chert: Light gray, sparsely developed.

III-8 Intermixed limestone and chert

Limestone: Light gray to light brownish gray; fossiliferous; medium grained; rough fracture; generally pure limestone.

Chert: Mottled light gray to white; replaces corals.

Description Column IV

IV-1a Limestone: Generally massively bedded (bedding thickness 1-1/2 - 4') with occasional shaly zones and laminations. Gray to dark gray.

Chert: Dark brown, thick (3-7") with thick (1-3") peripheral zone which weathers tan or buff. Chert beds are persistent and continuous because nodules are large and almost coalesced; spacing about 2" length about 1'. There are occasional zones of about the same total thickness as the large nodules (7") consisting of many closely spaced, elongated nodules and zone material. Chert most similar to #42.

IV-1b Limestone: Dark gray, weathers lighter gray, fine-grained, straight fracture, fossilferous. 1-1-1/2' beds, occasional thinly laminated shaly partings.

Chert: Brown with thin peripheral zone. Nodules 2-1/2 - 3" long, 2" thick, spacing 6-8".

IV-2 Thick section of essentially chert free limestone which appears to be very massively bedded but has indistinct bedding planes about 5-6" apart. Dark to medium gray where fresh, lighter gray where weathered. Medium grained and fossiliferous. Curved fracture planes and elongated fibrous fracture surface. The limestone is silty and argillaceous but massive with no shaly cleavage. Upon weathering, shaly character is more pronounced; prolonged weathering deteriorates the material to a clayey paste.

IV-3a Limestone: Fine grained, light to medium gray, smooth curved slightly fibrous fracture. Not obviously fossiliferous.

Chert: Dark brownish gray, fine line fractures. Several zones with persistent bedded character, and scattered nodules in between persistent zones. Many rounded, incompletely silicified zones.

IV-3b Interbedded chert and limestone, lithology generally as IV-3a above.

Limestone: Fine grained, smooth fracture, medium dark gray. Lower part is medium gray, fine grained, thin bedded "lensy" with interspersed black or dark gray chert.

Chert: Dark brown, thin peripheral zone, elongated stringers 1-3" thick, about 3-5" apart; resinous waxy luster.

IV-3c (Sample zone #501)

Massive unit of homogeneous lithology but with subordinate bedding planes.

Limestone: Medium gray, fine grained, apparently unfossiliferous. Elongated, splintery fracture with smooth, wavy surface.

Chert: Black to very dark gray, vertical, hairline cracks; thin peripheral zone may be present; subconchoidal fracture, resinous luster. Occurs in thin, persistent zones 3-4" thick, and 6-8" apart. The 3-4" unit will have one or more 1/2 - 1", elongated chert bands. Rounded nodules are interspersed between the zones of long nodules.

IV-4 Limestone: Thickness variable, massive, medium grained, light to medium gray, crystalline limestone, with sparsely distributed chert. Fossiliferous in lower part.

Description Column V

V-1 (Sample zone #38)

Limestone: Medium gray to dark gray, dense, homogeneous, fine-grained. Generally massively bedded (may reach 30-50" beds). Straight, blocky fracture with smooth, slightly curved fracture surfaces. Prominent stylolites in lower part. Chert is not abundant in this member.

Chert: Dark brownish black to black; sharp contact with matrix. No well developed peripheral zones. Fossiliferous, stylolites may define top and bottom of nodules and seams. Cherts occur as: (1) Persistent seams 4-5" thick, (2) Zones of rounded nodules 2-3" thick, 3-4" long, spacing between nodules 10-11".

V-2 Limestone: Gray, fine-grained, crystalline limestone, hackly fracture; some wavy shaly laminations.

Chert: Dark gray, sharp contact with matrix. Some scattered nodules of zone material showing no chert cores. Most similar to #42 type.

V-3 Limestone: The interval may be divided into four sections: (a), (b), (c), and (d). (a) and (c) are the same, and (b) and (d) are the same.

Section (a) Fine grained, gray limestone similar to Moorehouse except for more numerous and thicker (3-6") intervals of shaly limestone which is fissile and thinly bedded.

Section (d) Massive shaly and silty limestone with no pronounced shaly structure. That is, the limestone is argillaceous, but shaly character such as cleavage and fissility is not evident except when weathered. There are occasional "purer" intervals of medium to coarse grained, crystalline limestone, about 6" to 1' thick. Medium to dark gray, medium grained, fibrous elongate fracture.

Chert: Very sparsely developed, occasional incompletely silicified zones within the limestone.

V-4 Limestone: Coarse grained, (1.5 - 2mm) light gray, crystalline. Contains one interval of dark gray limestone similar to V-3d lithology above which carries nodules of dark gray to grayish black chert. No chert was noted in this, the Edgecliff component, in the drill core.

Description Column VI

VI-1 Limestone: Medium gray to bluish gray, even textured, fine grained crystalline limestone. Massively bedded but many stylolites form subordinate bedding planes. Smooth, slightly curved fracture surfaces.

Chert: Sparsely developed, occurs in thin, elongate lenses 1-2" thick occasionally coalesced to form thin, persistent beds. Dark brownish black, sharp contact with matrix; no peripheral zone, slightly calcareous.

VI-2 (Sample zone #42)

Limestone: Dark gray, even textured, homogeneous, dense, fine grained crystalline. Blocky fracture with rough, wavy fracture planes. Generally massively bedded with few subordinate bedding planes. Locally well developed shaly partings and occasional shaly laminations. Lithology more variable closer to Nedrow, (shaly and non-shaly in same bed).

Chert: Thick (3-6") bands (1-5' apart) many coalesced or almost coalesced to form continuous beds. Sharp contact with matrix. Peripheral zone absent or thin. Dark gray to grayish brown, fossiliferous, small hairline cracks, resinous luster. There are some intervals of lenticular, interbedded chert and limestone.

VI-3 Limestone: Argillaceous, dark gray, fine grained crystalline 12 to 15" beds; many subordinate bedding planes separated by thin shaly and silty partings. Generally chert free, but occasional small blebs of chert. One prominent zone of nodules.

Chert: Sparsely developed; one bed with zone of compound nodules and associated small round nodules. Dark brownish gray with buff or tan peripheral zone.

VI-4 Limestone: Massive, light gray, coarse grained, crystalline; rough fracture; occasional shaly parting.

Chert: Mottled, "35" type, light bluish gray interior, with dark bluish black exterior.

Description Column VII

VII-1 Limestone: Variably bedded; may be massive (24" beds) or thin-bedded with shaly partings. Medium dark gray, fine grained crystalline limestone with smooth curved fracture.

Chert: Sparsely developed; two thin (approx. 1" thick) but persistent beds of brownish gray chert with peripheral zone. Scattered nodules of zone material are also present.

VII-2 (Sample zone #34 and 35)

Limestone: Uniformly massively bedded, light gray to medium light gray, medium to coarse grained crystalline, (grain size 1-2mm). Fossiliferous; rough irregular fracture; locally has thin wavy shaly partings, and zones rich in fossil debris, particularly in lowermost section.

Chert: Nodular and compound nodular cherts outcropping along horizon; not coalesced, evenly spaced, sharp contact with matrix. No peripheral zone, but zone type material (incipient chert) distributed within chert. Nodules are 2-1/2 - 3" thick 5-6" long. Chert has resinous or waxy luster; is characteristically mottled in color with areas of medium and light bluish gray, and light and dark gray. Commonly has bluish black outer zone of irregular thickness. Above described chert is typically best developed in the lower portion of the member. In the upper portion of the member, smaller nodules may occur which are uniform in color and similar in properties to the light bluish gray component of the lowermost chert zones.

APPENDIX B

PETROGRAPHIC DESCRIPTIONS OF SIX CHERTS TESTED BY THE MORTAR BAR METHOD

Petrographic Descriptions of Cherts

Number 57—M_{89} $K_{.3}$ C_5 $Q_{.5}$ O_0 D_4 L_1

The groundmass of the chert is nearly colorless in plane polarized light and bright in x-nicols. It is composed primarily of even-grained, microcrystalline quartz (.005mm avg., range from .001-.009mm). Small local zones are commonly much finer grained, being composed of cryptocrystalline quartz (estimated grain size .001mm or less). Some of these zones are very nearly isotropic, brownish gray in plane polarized light and have a lower refractive index than the surrounding material. A few of these brownish areas contain spherulitic chalcedony. Other chalcedony is of the flamboyant and plumose variety and is restricted to vein filling. The areas of strongly varying texture are usually fossils which have been replaced by silica. A few fossils remain with carbonate interiors.

With the exception of these few incompletely replaced fossils there are no recognizable whole fragments of limestone. Calcite rich areas are present in the chert as localized concentrations of minute particles with high relief and high birefringence. Other mineralogic properties cannot be observed clearly because of the small grain size.

Dolomite is present as vein filling and as evenly distributed "floating" euhedra (.04mm ave. size, range from .008-.08mm).

There is no observable opal or isotropic silica. A small amount of pyrite occurs in local concentrations. Some detrital quartz grains are present which are distinguished from the chert groundmass by sharper outline due to slightly higher refractive index. They are sub-rounded to sub-angular, about .04mm in diameter and have sharp extinction.

Offsetting of veins indicates the following relative ages, from oldest to youngest: (1) chalcedony, (2) megaquartz or pseudoquartzite, (3) carbonate (dolomite and/or calcite). The widths of the veins are as follows: chalcedony .8-1mm, carbonate .16-.25mm, quartz .06mm. The occurrence of megaquartz or pseudoquartzite in this chert is restricted to vein filling.

Number 44—M_{80-85} K_5 C_3 Q_3 O_0 D_2 L_{1-2} plus pyrite about 1%

The groundmass is composed of microcrystalline quartz with finely divided carbonate (calcite?), and some larger (about .04mm) remnant limestone fragments. Evenly distributed dolomite rhombs (.04mm avg., range .008-.08) are present throughout the groundmass. In plane polarized light the chert is slightly clouded with light brownish gray material; in x-nicols the chert is generally

clear but with indistinct murky areas. The chert is variable in texture and grain size. Typical areas of microcrystalline quartz have an average grain size of .006 mm with a range from .003 to .009 mm. These areas grade into (1) local areas of coarser grain size (.011 mm avg.) with a greater range of grain sizes (.008-.032) and (2) local areas of dense, almost isotropic, cryptocrystalline quartz (grain size less than .001 mm) in which limestone fragments and dolomite rhombs appear to be floating.

Chalcedony is not abundant. Some occurs as fossil filling, and there are some brownish areas of colloform texture (1-2 mm in diameter) which contain fibrous and radial chalcedony. Veins contain (1) carbonate (calcite and/or dolomite) and (2) megaquartz. There are also small areas of megaquartz, (a) as fossil filling and (b) not obviously related to organic structures. No opal or isotropic silica was seen. Small grains of pyrite and a few detrital quartz grains are present in the chert.

The petrography is generally similar to No. 57, the chief difference is in the variability of texture and grain size.

Number 57-B--M_{80} K_0 C_0 Q_5 O_0 D_6 L_8 plus opaque less than 1%

The chert, generally clear in plane polarized light and with bright, pin point birefringence in x-nicols, is composed of a groundmass of uniform microcrystalline quartz (.005 mm avg., range from .0018 to .012 mm) in which are set dolomite rhombs (.05 avg., range .008-.13 mm) and ragged remnant limestone fragments about .03-.07 mm in diameter.

The principal variation of the texture is areas of pseudoquartzite which are much clearer than the surrounding groundmass in plane polarized light. Grain outlines may be distinguished in these areas in stopped down plane polarized illumination. The chert is vuggy in hand specimen and these areas of pseudoquartzite, some with mosaic texture, are considered to be microscopic vugs.

The contact between the areas of coarser quartz and the groundmass is sharp but irregular--the groundmass projecting into the vugs in rounded protrusions. The vugs are about .2 mm long with a range in length from .06 to .3 mm and are approximately 1/4 as wide as they are long. The grains in the vugs are equant in shape with irregular boundaries and about .104 to .008 mm in diameter. Because of the sharp contacts between the groundmass and the quartz, it was possible to note that the index of refraction of the groundmass is below that of quartz. (Chalcedony ?)

Local areas of finer grained, microcrystalline quartz occur but no cryptocrystalline quartz, opal, chalcedony, or vein material were seen. Minor components include detrital quartz grains (.05 mm avg. size, range from .04-.07mm) and opaque grains, white in reflected light possibly leucoxene. The detrital

quartz is coarser and more abundant than in 57 and 44. Some grains which occur in the adjacent limestone matrix have fine carbonate inclusions along the edges.

This chert differs from 57 and 44 in the abundance of the vug-like areas filled with coarser quartz, the absence of veins, cryptocrystalline quartz, and chalcedony.

Number 73--M_{80} K_5 C_2 Q_1 O_0 D_5 L_7 (There is a trace of "isotropic" silica which is probably not opal).

The groundmass is composed generally of uniformly grained microcrystalline quartz (.005 mm avg., range .002-.007) in which are set dolomite rhombs (.037 avg., .008-.1) and limestone fragments. The chert is variable in carbonate content and locally grades into areas which are incompletely silicified patches of limestone.

Rounded and elongate areas of dense cryptocrystalline quartz occur, which are darker brown in plane polarized light and very nearly isotropic in x-nicols. These areas are .08 to .28 mm in size, and many are obvious fossil fillings and replacements. There are also areas of very coarse microcrystalline quartz (.016-.04 mm) replacing fossil fragments, in which the grain outlines of the microcrystalline quartz cannot be distinguished in plane polarized light--as opposed to pseudoquartzite or megaquartz of comparable size in which they can be distinguished.

Poorly developed, spherulitic chalcedony is present in rounded darker brown areas about .06 to .12 mm in diameter. No plumose or flamboyant chalcedony was noted. There are some veins of carbonate and of quartz. Detrital quartz grains (subrounded, sharp outline, sharp extinction, .036 mm diam.) are present.

The chert is generally similar to 57 but differs in the presence of very calcareous areas.

Number 55--M_{79} K_3 C_1 Q_0 O_0 D_7 L_{10}

The groundmass, dusty in plane polarized light and murky in x-nicols, is composed of microcrystalline quartz (.006 mm avg., range .002-.010 mm) which contains dolomite euhedra (.04 mm avg., .016-.056), carbonate fragments, fossils and fossil debris, in various stages of silicification, and areas of cryptocrystalline silica.

The chert is crowded with carbonate fragments of about the same size as the microcrystalline quartz grains. Larger anhedral calcite fragments about .20 mm occur floating in the groundmass, and some large, incompletely silicified patches of limestone are present.

Dense, nearly isotropic, cryptocrystalline quartz occurs in a few darker brown (plane polarized light) areas about .12-.072 mm in diameter and is obviously related to fossil structures. Most fossils are replaced by coarse grained, microcrystalline quartz. A few of these are peripherally replaced by chalcedony. Otherwise, there are no large sectors of chalcedony.

Local areas of the chert have much unsilicified fossil debris. Veins of carbonate, probably dolomite, are present. There are minor amounts of detrital quartz grains (.04 mm avg.) and the opaque minerals pyrite and leucoxene(?).

The chert differs from the others in having no appreciable chalcedony or coarse quartz, and in having more abundant carbonate than the other cherts.

Number 45--M_{80} K_7 C_5 Q_3 $O_?$ D_2 L_3 (plus trace of an opaque mineral possibly pyrite)

The groundmass is colored (light brownish gray) but clear in plane polarized light and has bright, pin point, birefringent spots in x-nicols. It is generally composed of fine grained, microcrystalline quartz (average size about .003-.004 mm, with a range from .0018-.0072), but the texture is highly varied because of abundant replaced fossil fragments. A few fossils contain a little unreplaced carbonate. The usual dolomite rhombs (.04 mm avg., .008-.112 range) and grains of remnant limestone are present but in very small quantity and there is little finely divided carbonate dust which is usually present in the other cherts.

Areas of dense, cryptocrystalline quartz or isotropic silica differ from analagous areas in other cherts in that in plane polarized light they seem to have the same color and texture as the surrounding groundmass. These areas are about .20 mm in diameter and are apparently replaced fossils. A few show faint pin points of birefringence, but others are essentially isotropic. They are probably not opal since, as noted above, they are not distinguished by a difference in relief or texture from the groundmass.

There are no large sectors of chalcedony. Some radial, fibrous chalcedony is present replacing fossils, and some surrounds vugs filled with mosaic quartz. Pseudoquartzite replaces some elongate fossils. Detrital quartz grains are present.

This chert is the most siliceous and variable in texture of the group, and contains the most cryptocrystalline or isotropic silica.

APPENDIX C

HYPOTHESIS TO EXPLAIN REACTIVITY OF QUARTZOSE CHERTS

Hypothesis to Explain Reactivity of Quartzose Cherts

After the discovery of the alkali-aggregate reaction the early theories to explain the reactivity of siliceous materials towards alkalies were based upon the idea that the substances involved were all characterized by a certain instability at ordinary temperatures and pressures. Thus, substances viewed with suspicion were those silica minerals and mineraloids which were known to invert or grade into (change to) quartz, such as opal, natural and synthetic glass, cristobalite, tridymite, and chalcedony. The viewpoint which largely prevailed, as expressed by Mather (13), was that all those substances which can be described as "highly siliceous materials which are thermodynamically metastable at ordinary temperatures--silica not tied up in a cryatalline structure that is stable under normal ambient conditions," are potentially reactive. Ordinary quartz does not conform to this description.

During the 1950's some details of the constitution of chert forming minerals were illuminated. The hypothesis that chalcedony contained interstitial opal was discounted (22). Instead evidence was presented (6) which supported the idea that all properties of chert or chalcedony may be explained by a combination of quartz with water filled cavities. Midgely's (16)work enabled him to describe chalcedony and flint in much the same terms, i.e. the minerals are composed of a quartz network with a large number of micropores. The conclusion that chalcedony and microcrystalline quartz have the crystallographic structure of quartz does not help to explain their reactivity. Pelto (22) observed that pure, finely divided quartz does not react with alkalies to cause expansion and fracturing; hence the observed reactivity of chalcedony presents a problem.

Recent publications refer not only to the deleterious reactivity of microcrystalline quartz but also to deleterious reactivity of certain kinds of coarsely crystalline quartz.

With regard to the above Mielenz (18) says the following:

> "Typical fine-to coarse-grained quartz, either clear or milky, is not deleteriously reactive with cement alkalies. Typical expansion of moist-stored mortars containing high-alkali cement and quartzite or igneous quartz is in the range 0.01 to 0.04 percent at 1 year. It is interesting to note that the mortar bar data suggest that a low degree of reaction occurs in such specimens...
>
> Conversely, convincing evidence has recently been obtained to demonstrate that coarsely crystalline quartz which is intensely fractured, strained, and granulated internally as the result of metamorphic processes during geologic time, or which is charged with microscopical or submicroscopical inclusions, can cause a deleterious degree of expansion of mortar or concrete containing a high-alkali cement...Illite is common as inclusions in this type of quartz. The potentially deleteriously reactive

quartz particles typically are white or milky; however, not all white or milky quartz is deleteriously alkali-reactive. The petrographic or mineralogic criteria by which potentially deleterious crystalline quartz can be distinguished from innocuous quartz remain to be developed..."

The following hypothesis attempts to reconcile the lack of a deleterious degree of expansion of most quartz with the known deleterious expansion of quartzose cherts (of apparently the same mineralogic constitution as quartz) as established in this investigation and reported by others.

The mortar-bar expansion of normal quartz is at least 10% of the magnitude of expansion that we speak of when we refer to deleteriously expansive cherts. Quartz produces an expansion of about .033% at 12 months (17 p202-203). This figure needs to be multiplied by only 7 to be approximately equal to the maximum expansion of the chert observed in this investigation (.225%). Furthermore the quartz refered to above when subjected to the quick chemical test yielded an S_c of 31 mM/l of silica (R_c also 31) indicating that this material, described as coarsely crystalline quartz, is soluble in NaOH solution. The rose quartz tested in this investigation gave an S_c of 21, and an R_c of 42. (Table 6, and Figure) and hence S_c/R_c of .5, indicating that it, also, has a slight solubility in NaOH solution, but that it too would be considered innocuous.

As noted previously, the cherts investigated in this study give an X-ray pattern identical to that of the rose quartz used as a control aggregate. It is hereby suggested that the deleterious reactivity of quartzoae cherts is due to the natural small solubility of crystalline quartz in alkaline solutions, producing a slight degree of reactivity, which is increased many times by the greater internal surface area of the chert. Midgely (16) supplies the following data for the internal surface areas of some of the materials under discussion:

	Surface area in square cm/gm
Chalcedony	4,300
Flint	2,200
Opal	400,000
Quartz	0

It is necessary to assume that the materials which Midgely refers to as flint and chalcedony are similar to the microcrystalline quartz and chalcedony studied in this investigation. Chalcedony has a characteristic microscopic appearance and there should be little doubt as to its similarity, in all important respects, to the material to which the term was applied in this study. The term flint, if unqualified, in common parlance refers to a rock which may be composed of opal, chalcedony, microcrystalline quartz, or the other chert forming minerals previously described. Since opal and chalcedony are specifically mentioned separately it is reasonable to assume that Midgely's "flint" refers to a rock

composed essentially of microcrystalline and/or cryptocrystalline quartz. It seems also reasonable to assume that the internal surface areas of the cherts studied in this investigation, or in other investigations, might be somewhere in the neighborhood of 2 to 4,000 square cm/gm.

Consider 1 gram of quartz with internal surface area of zero or incrementally close to it. This has a minimal reactivity--S_C = 31, R_C = 31, S_C/R_C = 1, and .033% expansion at one year.

Let us take this gram of quartz and spread it out over 3,000 sq. cm. The surface area of this quartz is now let us say roughly, 10,000 to 100,000 times greater than the 1gm of solid quartz.[1] We now have a very large surface possessing a small but definite capacity for solution, particularly in environments of high pH.

The mortar bar expansion of quartz is approximately 10% that of chert, but the internal surface area of chert must be several hundred thousand times that of an equivalent amount of quartz. X-ray or other determinative tests may reveal only the presence of quartz, but X-ray analysis will not show that it is spread over a tremendous surface area.

In summary, the deleterious expansion of cherts which are found to be composed essentially of crystalline quartz may be due to the normal tendency of even crystalline quartz to dissolve slightly in alkaline solutions.

In addition, a certain amount of expansion may be contributed by the greater solubility of imperfectly formed, transitional, distorted, or amorphous regions within the chert. As an example of this type of irregularity, Pelto (22) suggested that crystallites in adjacent fibers of chalcedony may be joined by means of transitional structure. The transition is marked by dislocations or islands of bad fit which could accomodate impurities such as water. The presence of regions similar to these would increase the solubility of the chert.

In summary, the so called anomalous or irregular reactivity of cherts composed essentially of quartz should not be viewed as surprising. Since the effect of normal quartz spread over a large surface area is one factor contributing to expansion, and the effect of remnant, imperfectly developed or transitional regions is a second factor contributing to expansion.

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[1]It is not possible to divide by zero, but if the internal surface area of quartz is considered to be infinitely small, then the internal surface area of a chert may be considered to be infinitely greater than it.

APPENDIX D

SPECIFIC GRAVITY BY JOLLY BALANCE AND PYCNOMETER METHODS

Jolly Balance Method

In order to check on the accuracy and reproducibility of the method, a set of eight determinations was run on pure, homogeneous specimens of a mineral of accurately known specific gravity. Quartz of the rock crystal variety was selected for this purpose since it could also serve as a standard against which to compare the specific gravities of the cherts, which, according to x-ray analyses consist essentially of quartz.

Table 8 gives the values of specific gravity obtained for the rock crystal. The final result or mean value is given in terms of one standard deviation using (n-1)=7. Note that a temperature correction factor is used so that all values obtained are based on the maximum density of water at 4 deg. C. This procedure increases accuracy and assures that the results of a program of determinations made over a period of several months may be compared without regard to differences in the density of water during that period.

Specific Gravities by Pycnometer Method

In making a pycnometer determination the method, adopted from Dana (5), is as follows: The dry bottle with stopper is first weighed empty (P). The oven dried chert powder is introduced into the bottle and a second weighing (M) is made. The bottle is partially filled with distilled water and boiled for a few minutes to drive off any air bubbles. After cooling to room temperature the bottle is completely filled with distilled water and weighed (S). Care must be taken at this stage that the water rises to the top of the capillary opening; that there are no small bubbles present in the pycnometer; that the outside of the bottle is dry; and that the temperature of the contents of the bottle is approximately the same as the room temperature. The temperature of the contents is read from a thermometer which is built into the bottle stopper. The last weighing (W) is made after emptying the bottle and refilling with distilled water alone.

TABLE 8

Specific Gravity of Rock Crystal Quartz
by Jolly Balance Method

Values of s.g. uncorrected for temperature	X	Temperature correction factor	=	Corrected s.g. rounded off to 4 significant figs.	Deviation from mean value d	$d^2 \times 10^{-6}$
2.6608		.99823		2.656	.001	1
2.6611		.99823		2.656	.001	1
2.6633		.99780		2.657	.002	4
2.6610		.99780		2.655	.000	0
2.6627		.99780		2.657	.002	4
2.6682		.99732		2.661	.006	36
2.6625		.99732		2.655	.000	0
2.6530		.99732		2.646	.009	81
				2.655 Mean		127×10^{-6}

$$s.d. = \sqrt{\frac{d^2}{n-1}} = \sqrt{\frac{127 \times 10^{-6}}{7}} = 4.26 \times 10^{-3} = \pm .004$$

$$G = 2.655 \pm .004$$

To eliminate this last determination, for purposes of saving time and improving reproducibility, standard values were calculated for the weight of water in the pycnometer at various temperatures.

Since the last weighing (W) involves only the bottle filled with water, theoretically the only factor causing a change in this is temperature. Inasmuch as the pycnometer is a constant volume device i.e. it always holds the same volume of water, the weight of pycnometer plus water will be greater at a lower temperature than at a higher temperature due to the higher density of water at lower temperatures.

A total of 30 determinations of (W) were used to calculate accurately the volume of the two pycnometers used. The volume of the pycnometer in milliliters when multiplied by the density of water (gms/ml) at the desired temperature gives the weight of water. These values when added to the weight of the empty pycnometer (P) give the value for (W) at the temperature at which (S) was determined.

The specific gravity (G) can be computed from the relationship:

$$G = \frac{M - P}{W + M - P - S} \quad XL$$

Where L represents the density of the liquid. For routine work the factor L can be eliminated since the density of water is close to 1 throughout the normal range of working temperatures (20 - 30 deg. C). But for research purposes where a series of determinations are made over a long period of time, the results should be corrected for reasons stated previously.

In order to establish the limits of reliability of the pycnometer method and technique used in this study, and to establish a standard against which the cherts may be compared, several preliminary determinations with quartz were made.

For one series the quartz crystals which were used in the Jolly balance determinations were crushed to the size which would just permit the particles to pass through the neck of the pycnometer. This procedure maximizes the reproducibility of the method and substantially eliminates errors which may be introduced when 200 mesh powders are used. Such errors are caused by: (1) false weight for (M) due to chert or quartz dust not being completely wiped off the outside of bottle, (2) loss of material because of too vigorous boiling, (3) false weight for (S) because of small air bubbles due to incomplete boiling, (4) loss of very fine suspended material in overflow when placing stopper-thermometer. In short, the above procedure eliminates some variations in results due to poor technique and more accurately shows the limitations of the instruments. The results are shown in Table 9 - (1).

TABLE 9

Specific Gravity of Quartz by Pycnometer Method

(1) Coarsely Crushed Quartz

Values of G corrected for temperature and rounded to 4 significant figs.	Deviation from mean value d	$d^2 \times 10^{-6}$
2.647	.003	9
2.650	.000	0
2.651	.001	1
2.651	.001	1
2.649	.001	1
2.651	.001	1
2.650 mean		13×10^{-6}

Using (n-1) = 5 $\quad s.d. = \sqrt{\dfrac{13 \times 10^{-6}}{5}} = \dfrac{3.605 \times 10^{-3}}{2.236} = 1.61 \times 10^{-3}$

$G = 2.650 \pm .002 \qquad\qquad \simeq \pm .002$

(2) Minus 200 mesh Quartz Powder

2.652	.004	16
2.651	.003	9
2.647	.001	1
2.649	.001	1
2.654	.006	36
2.645	.003	9
2.646	.002	4
2.648	.000	0
2.641	.007	49
2.648 mean		125×10^{-6}

Using n = 9 $\quad s.d. = \sqrt{\dfrac{125 \times 10^{-6}}{9}} = \dfrac{11.180 \times 10^{-3}}{3} = 3.7 \times 10^{-3}$

$G = 2.648 \pm .004 \qquad\qquad \simeq \pm .004$

For the second series the coarsely crushed quartz crystal referred to above was pulverized as stated previously and a series of nine determinations run. This procedure more accurately shows what the expected deviations for the entire technique should be. The chert powders were treated in exactly the same manner so the results may be compared with the values for powdered quartz. The results of the quartz-powder determinations are shown in Table 9- (2).

Examination of Tables 8 and 9 shows that there has been an apparent slight reduction in the specific gravity of the same material from determinations done on the Jolly balance to the powder method of the pycnometer. A similar reduction in density was reported by Dale (4) who said that dry grinding (the method used in this study) caused a reduction in density of approximately .01. This reduction he attributed to inversion of part of the quartz to "vitreous" (amorphous) silica which has a lower density than quartz.

A more recent paper (23) contains a statement in support of that idea. In discussing the changes in properties of quartz caused by abrasion Siever says:

> "Indeed, it is the production of this surface layer (of amorphous silica) that is troublesome when pure quartz is wanted from a grinding operation. Van Lier has calculated that there is a disturbed layer about 300 A. thick on 2-5 micron quartz grains produced by grinding."

Perhaps the slight lowering of specific gravity noted in this study is due to an effect of this kind. Theoretically, the difference could also have occurred by chance.

APPENDIX E

THE CARBONATE EFFECT ON THE QUICK CHEMICAL TEST

The "Carbonate Effect" on the Quick Chemical Test

1. Increased R_c

Substances such as dolomite (including ferroan dolomite, magnesite, and siderite) have been shown to produce an anomalous increase in the reduction of alkalinity (R_c) and decrease in the concentration of silica. The result of such interference would be to shift data points in the deleterious area of the field upward and to the left (Fig. 15) where they might then be located in the innocuous area of the field. The reactions responsible for this are very probably of the following types; in which magnesite or dolomite react with the basic solution to produce an insoluble magnesium hydroxide:

$$MgCO_3 + 2NaOH \quad Mg(OH)_2 + Na_2\,CO_3 \qquad (2)$$

$$CaMg(CO_3)_2 + 2NaOH \quad Na_2CO_3 + Mg(OH)_2 + CaCO_3 \qquad (9)$$

The depressed values of dissolved silica which accompany this effect may be due to: (a) minimization of the attack on reactive forms of silica because of the reduction in alkalinity caused by the reaction, (b) insoluble products of the reaction (magnesium hydroxide or basic carbonate) acting as a protective film in limiting the attack of the solution on reactive forms of silica, (c) decomposition products of the reaction reacting with dissolved silica to form insoluble silicates, thereby removing silica from solution. (2)

Although all the cherts contain the minerals calcite and dolomite as established by petrographic examination, X-ray[1] and chemical analysis, those substances have not interfered with the tests to the extent of causing any chert to be classed as innocuous. However, it is possible that they have interfered to the extent of hindering reproducibility, or obscuring correlation between quick chemical and other results.

Sample No. 45 provides an interesting comparison since it had the highest S_c and R_c of any of the cherts, the highest percent silica, but the lowest percent CaO and MgO as determined by chemical analysis. The pertinent information is tabulated below. More complete chemical analyses will be found in Table 3.

1 No. 45 did not show any calcite or dolomite on the X-ray diffraction pattern but did show (lower than average amounts of) CaO and MgO in chemical analysis, and the minerals calcite and dolomite in thin-section, and on stained study slabs.

	Percent SiO_2	Percent CaO	Percent MgO
Average for[1] cherts excluding No. 45	88 (range 84-91)	4 (range 2-6%)	1 (range .8-1.5%)
No. 45	95	.7	.5

Comparison of the above data with Figure 15 shows that those cherts with the most dolomite and calcite did not cause a higher R_c than the chert with very little dolomite and calcite, and thus did not exhibit the "carbonate effect" by causing a spurious reduction in alkalinity.

2. Depressed S_c

The "carbonate effect" may have caused depressed values of dissolved silica in the tests under consideration.

Sample No. 45 was the most siliceous of the cherts analyzed chemically (95.14% SiO_2) and sensibly showed the highest S_c of any of the cherts. Five other cherts which among themselves have almost exactly the same silica content (90%, i.e. Nos. 44, 57, 73, 57-A, 57-B) showed variations of S_c from about 300 to 500. These cherts contained significant amounts of calcite and dolomite as shown by various tests, and may be exhibiting depressed values of dissolved silica. In Figure 32 percent silica is plotted against S_c.

Figure 32 shows a generally direct relationship between silica content of the cherts and S_c. The fact that five cherts, all of which have essentially the same silica content, show rather different values of S_c points to the influence of a lithologic factor. Possibly the "carbonate effect" either alone or in combination with other properties such as:

1) Varying percentages of the chert forming minerals--chalcedony, microcrystalline quartz, cryptocrystalline quartz,

2) varying grain size (and grain size distribution), porosity (and pore size distribution) between the above materials,

which would exercise a control on the capability of the cherts to release silica into solution.

It may be concluded that the carbonate effect has probably exercised little influence on the results of the quick chemical test with respect to spurious reduction in alkalinity. The carbonate effect may possibly have interfered with the values obtained for dissolved silica. At any rate, it has not influenced either S_c or R_c to the extent of causing any chert to be classed as innocuous.

[1] Eight of the nine cherts tested in mortar-bar.

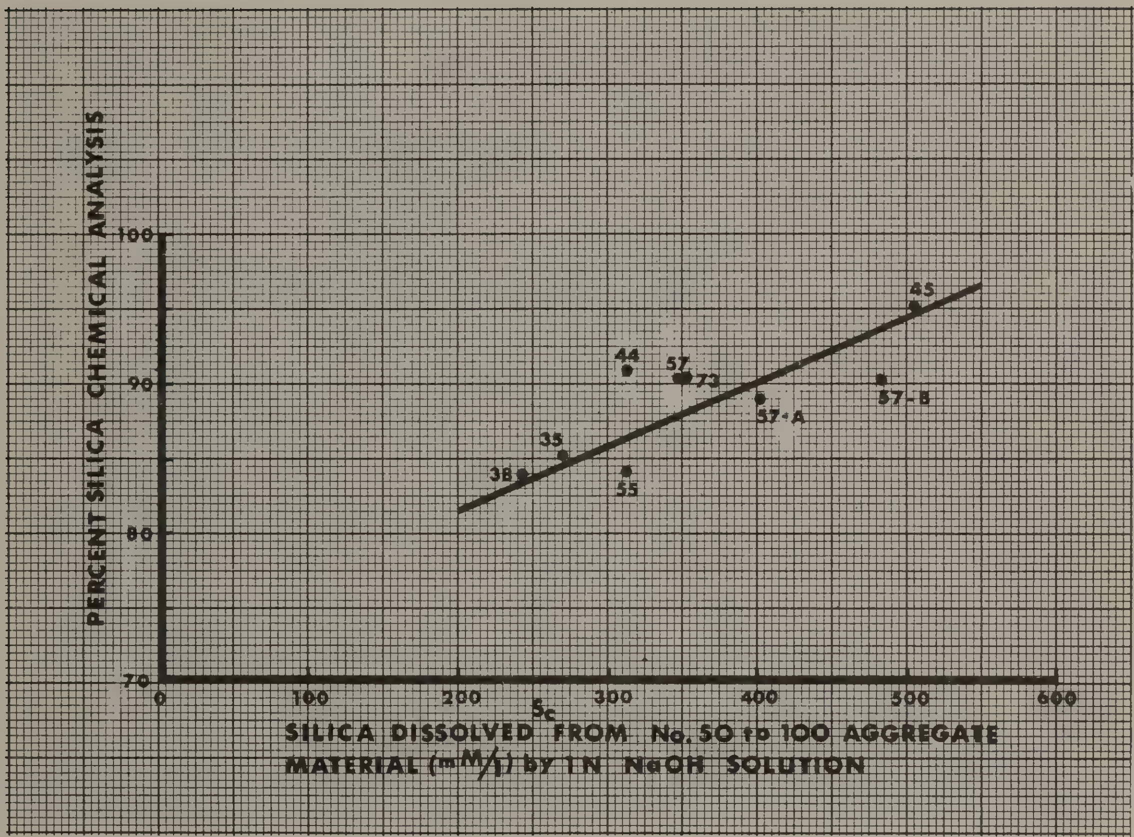

FIG. 32. SILICA DISSOLVED IN QUICK CHEMICAL TEST IS GENERALLY RELATED TO TOTAL SILICA CONTENT OF CHERTS.

APPENDIX F

CHEMICAL ANALYSIS OF CEMENT USED FOR FABRICATING THE MORTAR BARS

The following is the chemical analysis and physical test data for the four sacks of Type I cement which were used in fabricating the mortar-bars for the mortar-bar expansion test.

SiO_2	19.30%
Al_2O_3	6.98
Fe_2O_3	2.52
CaO	62.80
MgO	2.70
SO_3	3.05
Ign. Loss	1.20
	98.55

OK
WHS
8/2/91

Physical Tests

Fineness:
Blaine SA - 3650 Cm^2/gm
Air (c185) - 11.1%

Compound Composition:

C_3S	49.6%
C_2S	18.0
C_3A	14.2
C_4AF	7.7

The total alkalies, reported as Na_2O, were indicated by the supplier to be 1.06%. The alkalies were redetermined by the NYSDPW to be .89%, this figure was reported earlier as being the more correct figure for the total percent alkalies.